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VOL. 14, SEC. A.

JULY, 1936

NUMBER 7

THE SPECTRUM OF TREBLY IONIZED CERIUM¹

By R. J. LANG²

Abstract

The discovery of two members of the F series made it possible to obtain a fuller analysis of this spectrum. The following terms are located: 6S, 7S, 8S, 6P, 5D, 6D, 7D, 4F, 5F, 5G and 6G. Some thirty lines are classified. The deepest term, 4F, has an absolute value of approximately 296197 cm.⁻¹ based upon the three S terms and the use of a Ritz formula, giving an ionization potential of 36.5 volts.

In an earlier report (2) some of the more important terms in the spectrum of Ce IV were given, but at that time no F terms had been found and a fuller analysis could not be carried out. Two members of the F series have now been located together with three S, three D and two G terms.

The main interest in the analysis of this spectrum is connected with the 4f and 5d electrons. If the 4f electron is more strongly bound than the 5d then the deepest term in the spectrum will be 4F and not 5D as in the corresponding spectra Ti IV (5) and Zr IV (1). A decision in this matter had to await an investigation of the Ce III spectrum, which has now been carried out by Dr. H. N. Russell, and the writer is indebted to him for the location of the 4F-5D multiplet included in this report. Owing to the lack of confirmation of the F terms, the D terms presented in the previous report were incorrect. The line which was given as 6 P_{3/2}-6 D_{3/2} is a second order line. The new 6D terms are still puzzling, as there seems to be no reason for their inversion, but no other possibility could be found in the spectrum.

Table I shows the classified lines of Ce IV together with the wave numbers and intervals. The last column of the table shows the term values based upon 4F_{5/2}, which has been given zero value.

TABLE I
CLASSIFIED LINES IN CE IV

Combination	I.A. Int.	Wave number and interval	Term value
5 F _{7/2} - 7 D _{5/2}	2695.21 (9)	37092	4 F _{5/2} 0
5 F _{5/2} - 7 D _{3/2}	2693.44 (8)	37116	4 F _{7/2} 2253
5 F _{3/2} - 7 D _{1/2}		(37295)	5 D _{5/2} 49737
6 S _{1/2} - 6 P _{3/2}	2456.85 (45)	40690.4	5 D _{3/2} 52226
6 S _{1/2} - 6 P _{1/2}	2778.24 (90)	35983.5 4706.9	6 S _{1/2} 86602

¹ Manuscript received June 2, 1936.

Contribution from the Department of Physics, University of Alberta, Edmonton, Canada.

² Professor of Physics, University of Alberta.

TABLE I—*Concluded*
 CLASSIFIED LINES IN Ce IV—*Concluded*

Combination	I.A. Int.	Wave number and interval		Term value	
5 F _{5/2} - 5 G	2434.24 (3)	41080.6	201.5	6 P _{1/2} 122585	4707
5 F _{7/2} - 5 G	2446.24 (5)	40879.1		6 P _{3/2} 127292	
4 F _{5/2} - 5 D _{3/2}	2009.94 (100)	49736.6	2489.5	6 D _{3/2} 178913	-1715
4 F _{7/2} - 5 D _{5/2}	2000.42 (100)	49973.2		6 D _{5/2} 177198	
4 F _{5/2} - 5 D _{5/2}	1914.75 (35)	52226.1	4707	7 S _{1/2} 183502	201
6 P _{1/2} - 6 D _{3/2}	1775.30 (20)	56328		5 F _{5/2} 184545	
6 P _{3/2} - 6 D _{3/2}	1937.21 (10)	51621	-1715	5 F _{7/2} 184746	177
6 P _{3/2} - 6 D _{5/2}	2003.11 (35)	49906		7 D _{3/2} 221661	
6 P _{3/2} - 7 S _{1/2}	1779.03 (20)	56210	4707	7 D _{5/2} 221838	
6 P _{1/2} - 7 S _{1/2}	1641.58 (15)	60917			
5 F _{5/2} - 6 G	1572.62 (1)	63588	201	8 S _{1/2} 225128	
5 F _{7/2} - 6 G	1577.60 (2)	63387		5 G 225625	
5 D _{3/2} - 6 P _{1/2}	1372.72 (75)	72848	4707	6 G 248133	
5 D _{5/2} - 6 P _{3/2}	1332.16 (75)	75066			
5 D _{3/2} - 6 P _{3/2}	1289.41 (50)	77555	2489		
6 P _{1/2} - 7 D _{3/2}	1009.31 (5)	99077	4706		
6 P _{3/2} - 7 D _{5/2}	1057.67 (9)	94547			
6 P _{3/2} - 7 D _{3/2}	1059.64 (1)	94371	176		
6 P _{3/2} - 8 S _{1/2}	1022.12 (2)	97836	4707		
6 P _{1/2} - 8 S _{1/2}	975.20 (6)	102543			
5 D _{3/2} - 5 F _{5/2}	741.79 (40)	134809	2490		
5 D _{5/2} - 5 F _{7/2}	754.60 (30)	132520			
5 D _{5/2} - 5 F _{5/2}	755.75 (12)	132319	201		
4 F _{5/2} - 6 D _{5/2}		(177201)			
4 F _{7/2} - 6 D _{5/2}	571.59 (8)	174950			
4 F _{5/2} - 6 D _{3/2}	558.92 (8)	178916			
4 F _{5/2} - 5 G	443.11 (1)	225677	2253		
4 F _{7/2} - 5 G	447.58 (2)	223424			

The three S terms follow very closely the following Ritz formula

$$mS = \frac{16R}{[m - 2.9913 - 5.46 \times 10^{-7}(mS)]^2},$$

where m takes the values 6, 7 and 8. The absolute term values referred to the limit of this series together with the Rydberg denominators n are given in Table II.

TABLE II
ABSOLUTE TERM VALUES AND RYDBERG DENOMINATORS

Term value		n	Term value		n
6 S _{1/2}	209595	2.894	6 P _{1/2}	173612	3.180
7 S _{1/2}	112695	3.947	6 P _{3/2}	168905	3.222
8 S _{1/2}	71069	4.970			
5 D _{3/2}	246460	2.669	4 F _{5/2}	296197	2.435
5 D _{5/2}	243971	2.683	4 F _{7/2}	293944	2.444
6 D _{3/2}	117284	3.869	5 F _{5/2}	111652	3.966
6 D _{5/2}	118999	3.841	5 F _{7/2}	111451	3.969
7 D _{3/2}	74536	4.854	5 G	70572	4.988
7 D _{5/2}	74359	4.859	6 G	48064	6.044

In Ce III the $4f6s$ 3F 1F terms have as their limit the $4F$ terms of Ce IV, to which they converge in pairs in such a way that 3F_2 and 3F_3 approach the value 296197 cm.⁻¹ while 3F_4 and 1F_3 approach 293944 cm.⁻¹. There should, therefore, be approximate agreement in the intervals as shown below:

Ce III			Ce IV	
$4f6s$ $^3F_2 - ^3F_4$	2241		$4f$ 3F	2253
$4f6s$ $^3F_3 - ^1F_3$	2385			

The ionization potential of Ce IV based upon the deepest term, $4F_{5/2}$ is 36.5 volts. However, since all the similar ions shown in the last column of Table III have a D term for their deepest state, for comparison purposes in

TABLE III
IONIZATION POTENTIALS IN VOLTS

K I	4.32	Ca II	11.82	Sc III	24.6	Ti IV	43.0
Rb II	4.16	Sr II	10.98	Yt III	20.4	Zr IV	33.8
Cs III	3.87	Ba II	9.96	La III	19.1	Ce IV	30.4
		Ra II	10.10			Th IV	29.4

this table the potential for Ce IV is calculated on the basis of the $5D_{3/2}$ term. The data for Ra II is taken from the work of Rasmussen (4) and for Th IV from a paper by the writer (3). The remainder of the table is compiled from "Atomic Energy States" by Bacher and Goudsmit.

The table is typical of the beautiful symmetry that holds throughout the structures of these ions. A slight irregularity occurs at Ra II, or more probably at Ba II, the spectrum of which shows less regularity than that

of any other element listed in the table. Its D terms are irregular and its F terms beyond understanding. The most interesting thing shown by Table III is that it is possible to introduce eighteen *f* electrons into the structure without affecting the ionization potential measurably. The only effect so far discovered in this work is an increase in the width of the principal doublet intervals beyond the expected value in Ra II and Th IV (3).

Acknowledgment

It is a pleasure to thank Dr. H. N. Russell for his helpful advice and criticism during the progress of the work.

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A CONVENIENT MICROPROJECTION APPARATUS¹

By P. LAROSE²

It has been necessary to carry out in this laboratory during the last five years a large number of fibre diameter measurements, especially on wool, for which a special microprojection apparatus has been used. The novelty of this apparatus lies in the position of the ground glass screen relative to the microscope. The particular arrangement used has not been seen anywhere, and it possesses certain advantages for this type of work. It involves no new principle, but the geometrical disposition of the parts is such that it is very convenient where a large number of measurements have to be carried out under fairly high magnification, and the material on the stage of the microscope has to be moved frequently.

Fig. 1 is a photograph of the apparatus showing the position of the ground glass screen of the projection box relative to the remainder of the projection equipment, which is of a standard type. Only the ground glass part of the

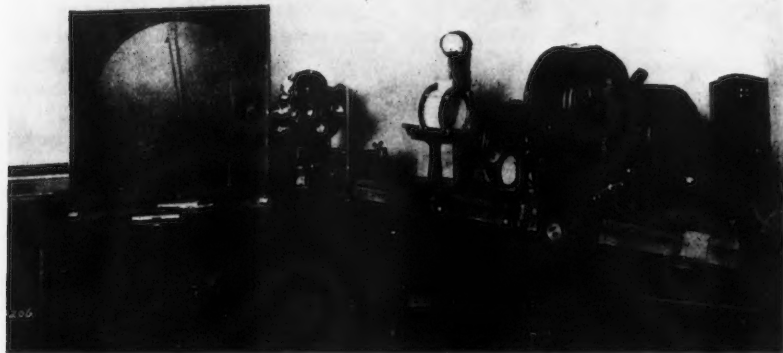


FIG. 1. Photograph showing relative positions of screen microscope and light source, and also size of field and image of wool fibre on the screen.

projection box is visible in Fig. 1, but Fig. 2 is a line drawing, to scale, showing the novel part of the apparatus, namely, the projection box. It consists of a metal casing shown in plan and side view in the figure. The back is open so as to admit a mirror, *M*, and the front is formed by a ground glass plate *S* which serves as a screen. The mirror that the writer uses is 8 in. in diameter, and the glass plate is 18 in. square. Both the glass plate and mirror are easily removable, the glass plate by sliding it out of the grooves formed

¹ Manuscript received June 2, 1936.

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada.

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by the turned-over edges of the metal casing on three sides, and the mirror by releasing four spring wires which hold it in position in the metal frame formed by the casing in the back. One of the sides of the casing has a re-

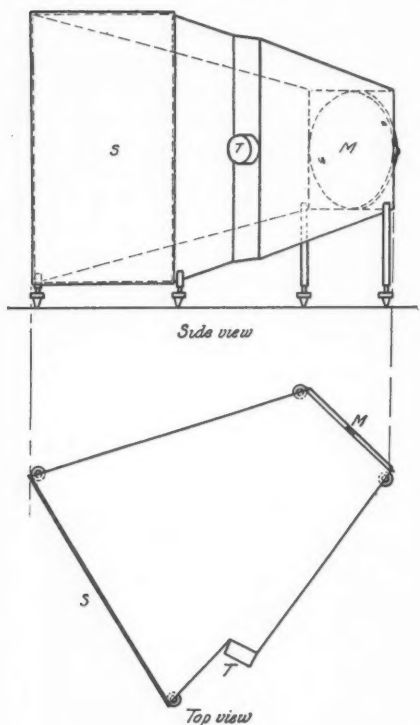


FIG. 2. Diagram showing construction of projection box.

entrant angle, and through one of the sides forming this angle is a circular opening flanged by a cylindrical collar T. The size of T is such as to admit the tube of the microscope, and the collar fits loosely into the sleeve of the adapter with which the microscope tube is provided. This arrangement prevents any extraneous light from entering the casing and at the same time allows easy focusing of the microscope. The casing is painted black both inside and out. The casing is so shaped that the angle of reflection is fairly small, about 15° . The metal casing stands on leveling screws which permit its height being adjusted to that of the microscope. The distance from microscope to mirror and back to screen is about 36 in., and with an objective of $20\times$ and a "Homal" of 20 mm. focal length, a magnification of 1000 is obtained. The circular field on the screen is then 15 in. in diameter.

The essential feature and advantage of this arrangement is that the operator can manipulate the focusing screws and those of the mechanical stage while sitting down comfortably and making his observations without the necessity

of employing remote focusing gear, which, as everyone who has used them knows, are not always convenient. This is of particular importance where a large number of measurements have to be made, and where the observations require frequent adjustment of the microscope either for focusing or for moving the stage.

In the case of fibre measurements, it has been found that six measurements a minute could easily be carried out where each measurement necessitated the bringing of another fibre (longitudinal view) into the field and the refocusing of the microscope.

There are on the market a number of instruments by means of which the image is produced directly on the screen or by reflection from a mirror, but, to the knowledge of the author, none of these possesses the advantage cited

above. The compactness of some of these instruments is such that the screen is much smaller, and for equal magnification would require a more powerful objective, and the resulting field would be much smaller.

In most of them, the screen is horizontal and in such a position that it is not convenient for a sitting observer. In many, the observer's head is in the path of the rays. This is a disadvantage. Finally, most of these instruments are designed for a definite purpose, sometimes with a narrow range of magnifications, and are constructed in one piece or with parts not interchangeable, so that they do not possess the advantage of the projection box described above, which is a complete unit by itself adaptable to all types of standard microscopes and projection apparatus.

The projection box described, although made of rigid metal, could easily be modified, if necessary, so that part of it is made like a camera bellows in order to allow a certain amount of focusing of the screen or mirror to permit the magnification being adjusted exactly to a desired figure.

AN ELECTRONIC SPEED GOVERNOR¹By B. G. BALLARD²

Abstract

Erratic performance of certain centrifugally governed electric motors prompted a search for a speed control that would be free from the effects of poor contacts, spring creepage, and friction in moving parts. These troubles were overcome by impressing a suitable alternating potential on the motor armature windings so that the rotor turned in synchronism with the alternating current system. The frequency of the latter was determined by a vacuum tube oscillator, and sufficient power obtained by amplifying the oscillator output with an inverter. Subsequent performance has proved very satisfactory.

Speed governors for direct current motors usually employ a centrifugally operated resistance control in the motor field circuit. Corroded or dirty contacts, spring creepage, and friction in moving parts are potential sources of trouble to which units of this and some other types are subject. Instances of trouble in such governors used on the driving motors of certain types of echo-sounding equipment had been brought to the author's attention. Also it had been observed that worn or improperly adjusted motor brushes had extended the governor setting beyond the normal range. Since accurate motor speeds are essential for accurate soundings, the development of a different type of governor was undertaken with the object of eliminating these sources of error as far as practicable.

The particular apparatus on which the investigation was carried out had previously given trouble owing to incorrect motor speed. To assist in compensating for the resulting error on the sounding chart, a motor speed indicator had been installed. It consisted of a frequency meter that was fed from two slip rings mounted on the motor shaft and connected to suitable bars of the commutator. Such an arrangement readily lent itself to the use of an electronic governor that would be largely free from the troubles previously mentioned. The speed would depend primarily on parts possessing relatively stable characteristics, such as condensers and inductances. As finally developed, the governor itself does not involve moving parts, and the adjustment or contact of the slip ring brushes has practically no influence on the performance. As for the main commutator brushes, actual tests have revealed that the governor will hold speed at the correct value even when they are lifted so as to break connection. However, satisfactory operation under this condition cannot be expected unless the slip ring brushes are making good contact. Unlike centrifugal governors the electronic governor is stable despite a strictly isochronous characteristic. Adjustment of the motor power input to accommodate changes in load is accomplished by a change in electrical phase angle.

¹ Manuscript received June 27, 1936.

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The sounding apparatus is used on a ship that is normally supplied with a 110 volt direct current service, and the electronic governor merely inverts the direct current to alternating current at a frequency determined by an oscillator. By connecting the alternating current circuit to slip rings, the motor is held "in step" in the same manner as a synchronous motor. Ordinarily the inverter supplies only sufficient power to maintain synchronism, but in an emergency can carry the entire armature load.

The circuit diagram is shown in Fig. 1. No attempt has been made to use a self-oscillating inverter circuit (1), since it was believed that a more constant frequency could be obtained from a separate oscillator.

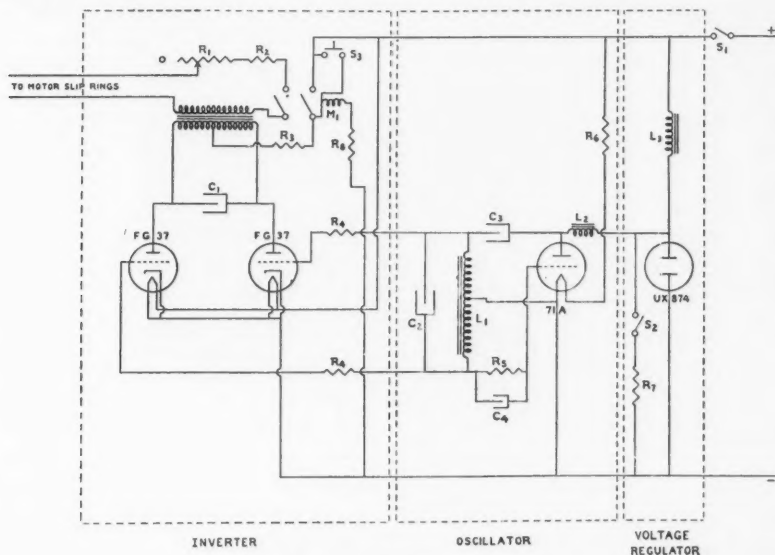


FIG. 1. Circuit diagram.

The required speed is 2880 r.p.m. and the motor, being bipolar, has a frequency of 48 cycles per second. Almost any type of grid-controlled gas-filled tube will invert at such low frequencies, but consideration of cathode heater voltages of available tubes suggested the use of the type FG-37 Thyatron, which operates on a positive grid. Positive grids draw comparatively large currents, thus imposing a heavy load on the oscillator, and for this reason a Type 71-A Radiotron is employed in the latter.

It will be noted that a voltage regulator has been introduced in the input to the oscillator to reduce the effects of variations in line voltage. The initial ionization voltage of the regulator tube is higher than the applied voltage, and discharge is initiated by impressing a surge from the inductance L_3 on the regulator tube terminals. The surge is generated by the opening of the

circuit containing resistor R_7 . L_2 serves the double purpose of preventing the transient from being dissipated in the oscillator circuit and of blocking the oscillations from the direct current supply circuit.

A contactor M_1 opens the inverter plate circuit in the event of failure of line voltage and prevents energization of plates before the cathode heater is connected.

The complete unit is shown in Fig. 2. No batteries are required and the only source of power is the 110 volt, d-c. supply. Connection to the motor is effected with two single leads, and the centrifugal governor can be retained



FIG. 2. Front view of governor.

without change if desired. An effort to make the operation reasonably fool-proof has influenced the design throughout. Electronic inverters frequently display a capricious behavior in starting, and sometimes fail to oscillate. Ordinarily when this occurs the line is short-circuited through one of the tubes, and the voltage drops too low to permit the second tube to function. However, the governor unit is provided with a resistor R_3 , which limits the short-circuit current to a safe value and protects the tube from injury. Inversion efficiency suffers, of course, but for low power applications the resulting protection easily justifies the increased losses.

As might be expected, the governor is effective only when the motor is locked "in step" with it. Once the speed becomes abnormal much of the corrective effort is lost, and the effect is not unlike an attempt to mesh two systems of gear teeth traveling at widely differing speeds. However, if a soft coupling is introduced between motor and governor the latter will assume control if the slip ring frequency and the oscillator frequency are not too widely

divergent. The rheostat R_1 provides such a coupling when the governor is first connected. Once correct speed has been established, R_1 is cut out so that the two systems are securely locked together.

It is interesting to note that the device operates whether power is fed from the inverter to the motor or vice versa. In the latter case the inverter becomes a rectifier, but it will rectify only a frequency corresponding to that of its grid excitation. Power flow from inverter to motor is preferable and subjects the motor to a lower electrical load.

Limits of Performance

Since oscillators operating at low frequencies are particularly sensitive to changes in line voltage, the output frequency may not always correspond to the natural period of the tank circuit. The voltage regulator tube reduces this error to a large extent. Line voltage variations of 10% cause a barely perceptible change in speed indication, and the accuracy of performance is still well within that of the remainder of the sounding gear.

Length of life of the inverter tubes imposes a very definite lower limit on line voltage. If the cathode emission falls below the demands for plate current, the cathode itself is subject to ionic bombardment, which soon destroys it. The cathode heater is rated at 115 volts and is connected directly across the 110 volt supply service. Emission varies approximately as the sixth power of the heater voltage, and since the actual plate current is not more than 40% of rated plate current, the lower limit of line voltage is $115\sqrt[6]{0.40}$, or 100 volts. Reasonable cathode life limits the upper range of voltage to 120 for the inverter tubes and 115 for the oscillator, assuming that the filament circuit for the latter is adjusted for a normal voltage of 110. For close speed control the line voltage should not vary more than 5% from normal.

Changes in temperature and humidity ordinarily encountered indoors give no observable error, and after a few weeks' operation the governor adjustment has displayed no tendency to creep. However, provision is made for changing the capacity of the tank circuit condensers should that prove necessary. Parts whose constancy might be affected by wide changes in temperature have been confined to a separate thermally insulated compartment.

It is, of course, possible to overload the inverter until it ceases to oscillate. Too strong or too weak motor field currents, excessive mechanical loads and too high or too low line voltages can cause such overloads. However, the design is believed to be adequate for all ordinary conditions that may arise. While the electronic governor successfully overcomes the deficiencies of the centrifugal governor, it must be admitted that the cost of component parts is relatively high. Nevertheless, the expense can be easily justified when it is realized that the accuracy and reliability of apparatus costing several thousand dollars is contingent upon the successful performance of the governor. Moreover, there is a possibility that in the future the cost of thyatrons, which now

constitute a major item of expense, may be reduced. The present limited commercial demand for the particular tube employed has precluded prices as low as those that generally prevail for equipment of this general class. Even now, tubes with similar characteristics and capacity and differing only in the voltage rating of the cathode heater are available on the market at a cost of only 35% of that of the Type FG-37 Thyatron. Either tube has considerably more capacity than the application requires, and as the demand for grid-controlled gas-filled tubes increases a more suitable type at an even lower price may be available.

Since the synchronizing torque is applied to the armature through the medium of a highly elastic magnetic field, it is to be expected that the elasticity combined with the inertia of the rotor will result in mechanical oscillations or "hunting"—a phenomenon that occurs quite frequently in synchronous machinery. The latter is usually provided with an "amortisseur" winding which effectively damps the oscillations, but the sounding apparatus motor was not so equipped. No evidence of hunting had been noted but a stroboscopic examination revealed a slight oscillation with a frequency of a few cycles per second. The addition of an external mechanical load increased the inertia and incidentally the period to such an extent that the oscillations became barely noticeable.

Other Applications

While the governor was developed primarily for echo-sounding equipment, it is equally applicable to other direct current motors. Its application would, of course, make it necessary to provide slip rings and associated brush gear unless the motor is driving a synchronous alternator, in which case the inverter may be connected directly to the latter. As mentioned previously, the governor described has a capacity considerably in excess of the demands, and it could control larger motors. The limit will depend on the degree of variation for which the governor is required to compensate. However, the fact that the control supplies an appreciable portion of the total power input to the motor should not be overlooked, and in larger capacities the cost would become excessive. Isochronous characteristics throw the entire load variation on the governor, since the motor does not change its speed so as to enable it to operate on some other point of its characteristic. For low power applications requiring extreme accuracy of speed control the electronic governor is unsurpassed. The setting is readily adjustable and if necessary the frequency can be held to closer limits than this particular application requires. Grid excitation for the inverter may be obtained from a tuning fork or a precise oscillator fully compensated for variations in temperature, humidity and line voltage. In the more powerful applications, hunting may present a problem unless the motor drives another machine provided with an "amortisseur" winding. Otherwise, it may be necessary to provide pole face dampers in the direct current machine.

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THE HYPERFINE STRUCTURE SEPARATIONS OF SOME TERMS IN THE THALLIUM II SPECTRUM¹

BY STANLEY SMITH² AND J. CONVEY³

Abstract

The hyperfine structure separations of about 25 terms of Tl II have been measured by means of two quartz and two glass Lummer plates used in conjunction with a Hilger E1 spectrograph. The light source was a hollow cathode discharge in helium. Large isotope displacements have been found in some of the terms of the $5d^96s^26p$ configuration, also in the $6p^2\ ^3P_2$ and $6p^2\ ^1D_2$ terms. The results have been used to calculate $g(I)$ and to examine the validity of the application of the summation rules to the separation factors for the $6snd$ and $6snf$ configurations. The spacing of the system of levels arising from the $6s6f$ configuration has been examined.

The multiplet structure of the Tl II spectrum was first dealt with in papers published in 1928 (7, 11, 14). A more detailed account of the multiplet structure and some measurements of the hyperfine structure were given in a paper by McLennan, McLay and Crawford (8). An extension of the classification of the spectrum, together with some further h.f.s. data, was published by Smith (15). Using a three metre concave grating of 60,000 lines, McLennan and Crawford (6) were able to investigate with greatly improved accuracy the h.f.s. of the Tl II lines. Later Schüller and Keyston (13), by means of a Fabry and Perot interferometer, determined with still greater accuracy the h.f.s. intervals of 10 of the terms, and dealt with some cases of isotope displacement of h.f.s. levels. Recently Ellis and Sawyer (2) have made a large extension of the series classification, identifying 35 new terms, including some of the terms arising from the configuration $5d^96s^26p$. In the present investigation the h.f.s. of more than 20 terms, other than those already investigated by Schüller and Keyston (13), have been measured by means of two quartz and two glass Lummer Gehrcke plates used in conjunction with a Hilger E1 spectrograph. The h.f.s. separations of more than 30 terms of Tl II may now be regarded as known to a fairly high degree of accuracy.

Experimental

The light source was a hollow cathode discharge in helium at a pressure of about 7 mm. of mercury. The electrodes, consisting of an inner cylinder of molybdenum, which held the thallium, and an outer cylinder of aluminium, were enclosed in a Pyrex glass tube immersed in a bath of running cold water. The discharge was excited by a d-c. dynamo generating about 900 volts.

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With suitable resistance in the circuit, the current through the tube was adjusted to a value of about 0.25 amp. The light emerged from the tube and the water bath through quartz windows. It was focused by means of a quartz lens on the reflecting prism of the Lummer plate. A quartz fluorite lens of focal length 23 cm. projected the interference fringes on the slit of the spectrograph. The Lummer plate was housed in a double walled box of heat insulating material, the inside temperature of which was controlled by a thermostat. The room temperature was also under thermostatic control. The Lummer plate was carefully adjusted so that the fringes from the top and bottom of the plate respectively were approximately of the same intensity and symmetrically disposed with respect to the centre of the slit of the spectrograph. Two quartz Lummer plates were used, each of length 13 cm. and of thickness 0.4493 cm. and 0.5825 cm. The thinner plate had its optic axis parallel to the long edge of the plate. A Nicol prism placed between the source and the plate allowed light with its electric vector parallel to the plane of the plate to fall on the plate so that the light passed through it as ordinary rays. The thicker plate had its optic axis parallel to the short edge of the reflecting face of the plate, and the plane polarised light from the Nicol prism passed through the plate as extraordinary rays. The two glass plates used had the following dimensions: length, 13 cm. and 20 cm.; thickness, 0.4872 cm. and 0.6198 cm. respectively. Eastman Process Panchromatic and Eastman 33 photographic plates were used. They were developed in Agfa fine grain developing solution.

The interference patterns were measured on a comparator reading to 0.001 mm and the h.f.s. separations were calculated by using the double fringe pattern according to the method of McLennan and McLeod (9).

Experimental Results

For many of the less intense combinations, the h.f.s. patterns were incomplete owing to the absence on the plates of the weaker h.f.s. components. In such cases it is clear that the measures will not give the h.f.s. separation of both terms of the combination, and only if one separation is already known can the other be computed. In dealing with these incomplete patterns, the h.f.s. separations found by Schüller and Keyston (13) were used as much as possible. Tables I and II present the results of the measurements of the combination: observed in this investigation.

The top number in each compartment is the h.f.s. separation in $\Delta\nu 10^{-3} \text{ cm.}^{-1}$ of the term at the head of the column; the bottom number is the h.f.s. separation of the term at the left of the row; and the central number is the approximate wave-length of the combination in Ångstrom units. The square

bracket enclosing a separation in any compartment indicates that the value of that separation has not been deduced from the measurements of that particular term combination.

TABLE I
H.F.S. SEPARATIONS OF Tl II TERMS

Term	$6s7p\ ^3P_0^o$	$6s7p\ ^3P_1^o$	$6s7p\ ^3P_2^o$	$6s7p\ ^1P_1$	1_2^o	4_2^o
$7s7d\ ^1D_2$		[4015] 5774 616				
$6s7d\ ^3D_1$	0 5384 -2204	4030 5447 -2209				
$6s7d\ ^3D_2$		4016 5410 761		[-1277] 6378 763		
$6s7d\ ^3D_3$			*[3472] 6180 3373		615 †3593 [3373]	
$6s9s\ ^3S_1$	0 3837 4550		*[3472] 4274 4550			
$6s9s\ ^1S_0$		4021 3843 0		-1277 4307 0		
$6s8d\ ^3D_1$	0 3540 -2305	4012 3567 -2302	*[3472] 3909 -2298			
$6s8d\ ^3D_2$		4015 3560 1627	*[3472] 3901 1626	-1276 3955 [1627]		
$6s8d\ ^3D_3$			*[3472] 3887 3414			*[642] †4481 3432
$6s8d\ ^1D_2$		[4015] 3460 - 504		[-1277] 3832 -511		
$6s8s\ ^3S_1$					615 †4312 5310	
$6p^3\ ^1D_2$		[4015] 4462 - 826		[-1277] †5099 - 815		

*Value given by Schüller and Keyston (13).

†Isotope shift observed for this combination.

TABLE II
 H.F.S. SEPARATIONS OF TI II TERMS—(Continued)

Term	6s7s 3S_1	6s7s 1S_0	6s6d 1D_2	6s6d 3D_1	6s6d 3D_2	6s6d 3D_3	6p 2 3P_2	6s10s 3S_1
6s5f $^3F_3^o$						3332 5183 *[675]		
6s5f $^3F_4^o$						[3332] 5152 3290		
6s5f $^1F_3^o$						3356 5143 [1480]		
10 o_3			*[834] †3619 624		*[555] †3794 623	[3332] †3852 592		
6s6f $^3F_4^o$						[3332] 3369 3524		
6s6f $^3F_2^o$				*[-2121] 3291 -2775	*[555] 3322 -2782			
6s6f $^3F_3^o$					*[555] 3321 -2282	[3332] 3365 -2283	546 †5643 [-2282]	
6s6f $^1F_3^o$					*[555] 3320 2955	[3332] 3364 2957	569 †5640 [2956]	
7 o_2	*[4980] †4177 1122							5910 4460 [1122]
8 o_1		0 †3791 281	*[834] 5206 305					
12 o_2			*[834] †3339 1270			[3332] †3536 1267		
6s7f $^1F_3^o$							[557] †4286 695	

*Value given by Schüller and Keyston (13).

†Isotope shift observed for this combination.

Isotope displacements were observed in many cases. They will be discussed in a subsequent paragraph.

In Table III will be found the mean value of the h.f.s. separations and the separation constants. The term classification of Ellis and Sawyer has been used throughout. As there have been changes in the classification of several of the terms from time to time, it was thought advisable to include the term

values in the table, the normal state $6s^2 {}^1S_0$ being taken as zero. For the sake of completeness, the h.f.s. separations already found by Schüller and Keyston are also given.

TABLE III
SEPARATION FACTORS OF Tl II TERMS

Term	Term value in cm^{-1}	H.f.s. separation in 10^{-3} cm^{-1}	Separation factor	Term	Term value in cm^{-1}	H.f.s. separation in 10^{-3} cm^{-1}	Separation factor
$6s7s {}^3S_1$	105,225	4980*	3.320	$6s5f {}^1F_0^o$	136,263	1480*	.423
$5d^9 6s^2 6p {}^1P_2^o$	110,387	615 ± 7	$.246 \pm .003$	$6s7d {}^1D_2$	136,891	614 ± 10	$.246 \pm .004$
$6s6d {}^1D_2$	115,160	834*	.334	$6s7d {}^3D_1$	137,927	-2206 ± 3	$-1.471 \pm .002$
$6s6d {}^3D_1$	116,147	-2121*	-1.414	$6s7d {}^3D_2$	138,053	762 ± 5	$.305 \pm .002$
$6s6d {}^3D_2$	116,430	555*	.222	$6s7d {}^3D_3$	138,203	3373 ± 5	$.964 \pm .002$
$6s6d {}^3D_3$	116,826	3332 ± 4	$.952 \pm .001$	$6p^2 {}^1D_2$	141,982	-820 ± 5	$-.328 \pm .002$
$6s7p {}^3P_1^o$	119,576	4015 ± 4	$2.677 \pm .003$	$5d^9 6s^2 6p {}^10P_2^o$	142,781	613 ± 13	$.175 \pm .004$
$6s7p {}^3P_2^o$	122,029	3472*	1.389	$5d^9 6s^2 6p {}^12P_2^o$	145,092	1268 ± 6	$.507 \pm .002$
$6s7p {}^1P_1^o$	122,379	-1277 ± 3	$-.851 \pm .002$	$6s9s {}^3S_1$	145,415	4550 ± 4	$3.033 \pm .003$
$5d^9 6s^2 6p {}^4P_2^o$	125,437	642*	.257	$6s6f {}^3F_4^o$	146,500	3524 ± 2	$.783 \pm .001$
$5d^9 6s^2 6p {}^5P_1^o$	126,204	-203*	.135	$6s6f {}^3F_2^o$	146,523	-2778 ± 4	$-1.111 \pm .002$
$6p^2 {}^3P_2$	128,817	557 ± 12	$.223 \pm .005$	$6s6f {}^3F_3^o$	146,534	-2282 ± 3	$-.652 \pm .001$
$5d^9 6s^2 6p {}^7P_2^o$	129,158	1222 ± 4	$.489 \pm .002$	$6s6f {}^1F_3^o$	146,543	2956 ± 4	$.845 \pm .001$
$6s8s {}^3S_1$	133,568	5310 ± 10	$3.540 \pm .007$	$6s8d {}^3D_1$	147,602	-2303 ± 2	$-1.535 \pm .001$
$5d^9 6s^2 6p {}^8P_1^o$	134,362	281 ± 2	$.187 \pm .001$	$6s8d {}^3D_2$	147,652	1627 ± 2	$.651 \pm .001$
$6s5f {}^3F_3^o$	136,115	-675*	-.193	$6s8d {}^3D_3$	147,747	3423 ± 9	$.978 \pm .003$
$6s5f {}^3F_2^o$	136,216	-2477*	-.991	$6s8d {}^1D_2$	148,465	-508 ± 6	$-.203 \pm .002$
$6s5f {}^3F_4^o$	136,230	3290 ± 10	$.731 \pm .002$	$6s10s {}^3S_1$	151,568	5910 ± 40	$3.940 \pm .027$

* Value given by Schüller and Keyston (13).

The estimated errors are included in Table III. The chief source of error in the case of the larger separations lies in uncertainties in the calculated constants of the Lummer plates. This may be illustrated by considering the individual measurements of the h.f.s. separation of $6s9s {}^3S_1$. The separation was found by using the combinations $6s7p {}^3P_0 - 6s9s {}^3S_1$ ($\lambda 3837$) and $6s7p {}^3P_2 - 6s9s {}^3S_1$ ($\lambda 4274$). In the latter, Schüller and Keyston's value for the $6s7p {}^3P_2$ separation, viz., $3472 \text{ cm}^{-1} \cdot 10^{-3}$ was used. The measures are shown in Table IV.

TABLE IV
COMPARISON OF MEASUREMENTS OF H.F.S. SEPARATION OF $6s9s {}^3S_1$

$\lambda 3837$			$\lambda 4274$		
Quartz Lummer plate, mm.	Photo-graphic plate	$\Delta\nu$ in 10^{-3} cm^{-1}	Quartz Lummer plate, mm.	Photo-graphic plate	$\Delta\nu$ in 10^{-3} cm^{-1}
4	1	4548	4	1	4546
4	2	4545	4	2	4546
6	3	4554	4	3	4546
6	4	4553	6	4	4556
			6	5	4555

The values obtained from the 6 mm. plate are consistently larger than those derived from the 4 mm. plate. In the 6 mm. plate the extraordinary ray was used and the optical constant of the plate was calculated (16) by using the formula for the refractive index given in Drude's Theory of Optics (1, p. 391). For the 4 mm. plate the ordinary ray was used and a Cauchy formula was applied to calculate the optical constant. In the 4 mm. plate interference pattern the two components overlapped by five orders, and for the 6 mm. plate the overlapping was greater still, being about seven orders. Hence a small error in the fifth significant figure in the optical constant will cause an error in the fourth significant figure in the computation of the h.f.s. separation of $6s9s\ ^3S_1$. In general the results from the glass Lummer plates were less accurate than those obtained from the quartz plates. This is without doubt due to the scanty refractive index data available for these plates. For the 4 mm. glass plate the refractive indices for the C, D, F and G lines were known to the fifth significant figure. For the 6 mm. plate the indices were given to the sixth significant figure for C, D and F only, so that for wave-lengths less than $\lambda 4861$ the Cauchy formula had to be extrapolated.

Isotope Displacement

Discussion

Schüler and Keyston found that in two of the terms investigated by them the h.f.s. levels of the less abundant isotope of Tl (mass number 203) lay considerably below the corresponding levels of the other isotope. The two terms showing this large displacement were designated as $6s7p\ ^1P_1$ and X_2 . Ellis and Sawyer (2) have classified both these terms as belonging to the $5d^96s^26p$ configuration and have named them 5^0_1 and 4^0_2 respectively. For 5^0_1 it was found by Schüler and Keyston that the h.f.s. separation was the same for both isotopes; viz., 0.203 cm.^{-1} , but for 4^0_2 the separation for isotope 205 was 0.642 cm.^{-1} , and for isotope 203 it was 0.637 cm.^{-1} . The line $\lambda 4736$ ($6s6d\ ^1D_2 - 6s5f\ ^1F_3$) also showed an isotope displacement of 0.045 cm.^{-1} , due presumably to the $5\ ^1F_3$ term. In the present investigation five additional terms arising from the $5d^96s^26p$ configuration are found to exhibit considerable isotope displacement, as do also $6p^2\ ^3P_2$ and $6p^2\ ^1D_2$. It is significant that all these terms arise from configurations that contain completed $6s$ systems.

10^0_3 . Three lines involving this term have been investigated; viz., $\lambda 3794$, $\lambda 3852$ and $\lambda 3619$. The systems of levels are shown in Fig. 1, the arrows denoting the observed components. The intervals are given in $\Delta\nu 10^{-3}\text{ cm.}^{-1}$. In Figs. 1 to 5 the full horizontal lines refer to the 205 isotope and the dotted lines to the 203 isotope. The fine structure quantum number is placed to the left of the corresponding level. Only the h.f.s. separations and the isotope displacements are drawn to scale.

For $\lambda 3619$, b' was not found, hence the position of the lower of the two 10^0_3 levels for isotope 203 could not be established.

12_2^0 . An isotope displacement was observed in the lines $\lambda 3339$ and $\lambda 3536$ involving 12_2^0 , and is shown in Fig. 2A and Fig. 2B. In each case only one component belonging to the 203 isotope was observed, so that the h.f.s. separation of the levels of 12_2^0 for the weaker isotope could not be found.

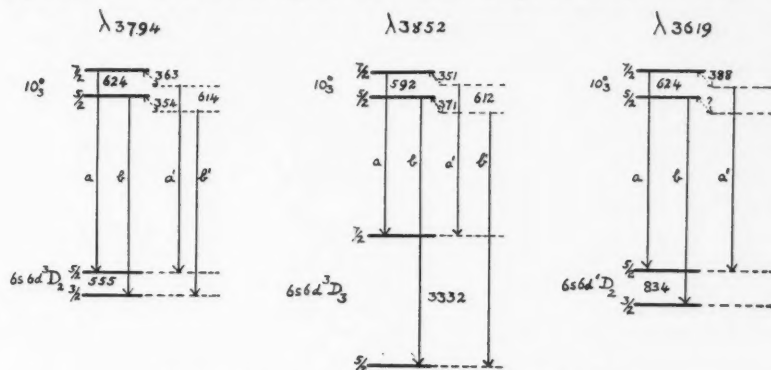


FIG. 1. Systems of levels for $\lambda 3794$, $\lambda 3852$ and $\lambda 3619$.

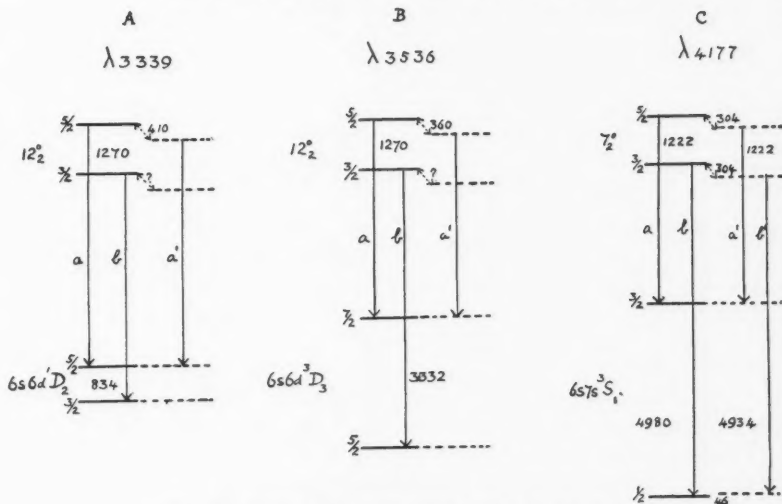


FIG. 2. Systems of levels for $\lambda 3339$, $\lambda 3536$ and $\lambda 4177$.

In Fig. 2A and Fig. 2B it will be noticed that the wave number difference $a - a'$ is smaller for the 3D_3 combination than for the 1D_2 combination, as is also the case when 10_3^0 is in combination with the same D terms. This seems to indicate that the upper h.f.s. level of the 1D_2 term for isotope 203 lies a little below the corresponding level for the 205 isotope.

7_2^0 . Fig. 2C represents the combination of this term with $6s7s\ ^3S_1$.

It was found that $a - a' = 304$ and $b - b' = 350$. Schüller and Keyston had previously noticed that for $7\ ^0\text{S}_1$ the separation for the 203 isotope was less than that for the 205 isotope by 45. The measurements on $\lambda 4177$ lead to the value 46 for this difference if it is assumed that the separations of the $7\ ^0_2$ levels are the same for both isotopes.

$1\ ^0_2$. The lines $\lambda 3593$ and $\lambda 4312$ involving this term have been investigated and the level systems are given in Fig. 3A and Fig. 3B.

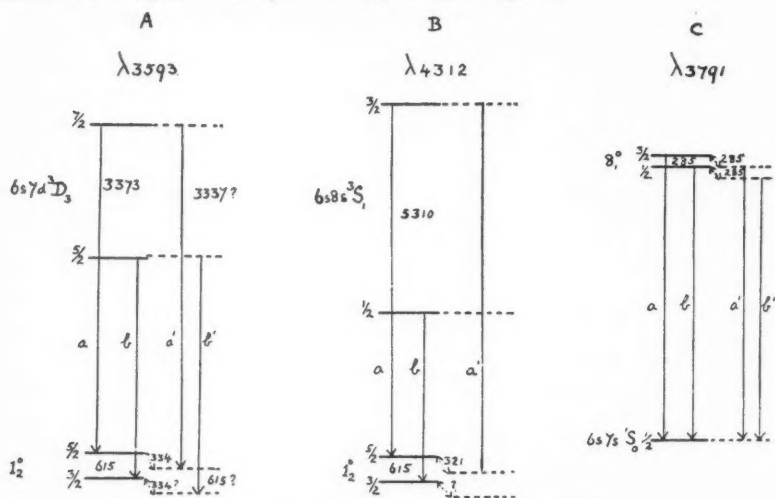


FIG. 3. Systems of levels for $\lambda 3593$, $\lambda 4312$ and 3791

For $\lambda 3593$, the measurements gave $a' - a = 334$, and $b' - b = 370$. As it is unlikely that the separation for the 203 isotope is greater than for the 205 isotope, the separation of $7\ ^0\text{D}_3$ for isotope 203 is probably not greater than 3337. For $\lambda 4312$, $a' - a = 321$, but b' unfortunately was missing on the plates.

$8\ ^0_1$. The line $\lambda 3791$ has three components on three of the plates measured. Two of the components, α and β , were strong and of almost equal intensity, the remaining component, γ , being weak. The interpretation of the data is given in Fig. 3C.

The measurements gave $\alpha - \beta = 285$, and $\alpha - \gamma = 567$. If the isotope displacement is taken to be 285, and the separation also 285, then b and a' would be superimposed on the plates, giving component β ; γ would then be b' . The theoretical intensity ratio of α , β and γ would be 100 : 94 : 22, making α and β of almost the same intensity. It is of course quite probable that b and a' are not exactly coincident, and that the upper $8\ ^0_1$ level for isotope 203 lies a little below the lower level for isotope 205, thus making the separation for the 203 isotope a corresponding amount smaller than that for the 205 isotope.

$6p^2\ ^3P_2$. The line $\lambda 4286$ gives four components identified as shown in Fig. 4A.

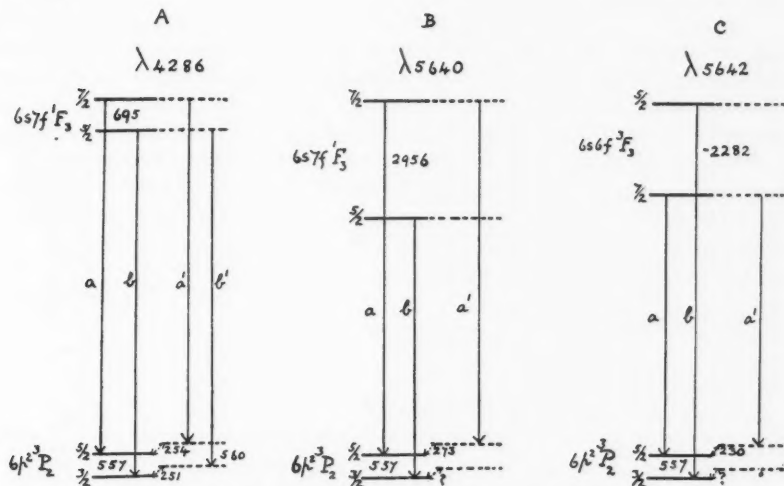


FIG. 4. Systems of levels for $\lambda 4286$, $\lambda 5640$ and $\lambda 5642$.

If this assignment is correct, then the h.f.s. levels of $6p^2\ ^3P_2$ for the isotope 203 lie above those of isotope 205. That this is the case is suggested also by the combinations of $6p^2\ ^3P_2$ with $6s6f\ ^1F_3$ and $6s6f\ ^3F_3$, which give the lines $\lambda 5640$ and $\lambda 5642$ respectively. Owing to the low dispersion in this region, the interference patterns of the two lines are somewhat mixed and difficult to interpret. The schemes deduced are given in Fig. 4B and Fig. 4C.

The lack of agreement between the two displacements; *viz.*, 230 and 273, of the upper level of $6p^2\ ^3P_2$, may be due to inaccuracy in measurement or to isotope displacements in the 6F h.f.s. levels. The average of 230 and 273 agrees very closely with the displacement found in $\lambda 4286$.

$6p^2\ ^1D_2$. The line $\lambda 5099$ shows an isotope displacement. The components belonging to the weaker isotope unfortunately appeared on only one plate, consequently giving rise to an ambiguity in the interpretation. The more plausible interpretation is given in Fig. 5.

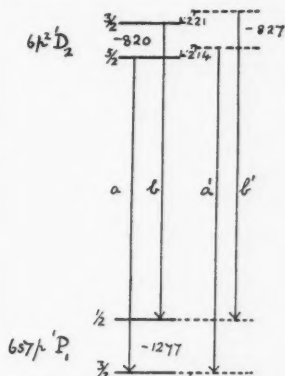


FIG. 5. System of levels for $\lambda 5099$.

The alternative interpretation would bring the $6p^2\ ^1D_2$ levels for isotope 203 below those of the 205 isotope by 658 and 651. In view of the large value of

such a displacement and the fact that its direction would be opposite to that deduced for the $6p^2\ ^3P_2$ term, the interpretation here chosen seems to be the more probable one.

Application of the Summation Rules

Goudsmit (4) has shown how the separation factors of terms arising from two valence electrons can be expressed as linear functions of the separation factors of the individual electrons for the two extreme cases of (*jj*) coupling and Russell Saunders' coupling. However, if the coupling is intermediate, then the summation rules have to be applied. If all the separation factors of the terms arising from an *sd*. or an *sf*. configuration are known, then two separate determinations (16) of $a' + a''$ can be made, where a' and a'' denote the separation factors of the non-*s* electron for $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$ respectively. Applying this method to the *6snd* and *6snf* configurations of Tl II, the results shown in Table V are obtained.

TABLE V
SUM OF SEPARATION FACTORS OF *nd* AND *nf* ELECTRONS IN Tl II

Configuration	Values of $a' + a''$	Configuration	Values of $a' + a''$
<i>6s6d</i>	0.047 0.107	<i>6s5f</i>	-0.015 ± 0.002 -0.014 ± 0.003
<i>6s7d</i>	0.022 ± 0.005 0.091 ± 0.014	<i>6s6f</i>	-0.068 ± 0.002 -0.057 ± 0.003
<i>6s8d</i>	-0.055 ± 0.003 -0.055 ± 0.014		

It is interesting to note that in the *6snd* series the largest discrepancy between the two values of $a' + a''$ occurs for the *6s7d* configuration. This is to be expected for Ellis and Sawyer (2) have pointed out that the *6snd* 1D_2 terms are perturbed by $6p^2\ ^1D_2$, and that the perturbation is a maximum for *6s7d* 1D_2 . On the other hand, the close agreement between the two values of $a' + a''$ for the *6s8d* configuration is rather surprising in view of the fact that *6s8d* 1D_2 is distinctly perturbed by $6p^2\ ^1D_2$. The perturbation of the *6s5f* $^3F_{2,3}$ and *6s6f* $^3F_{2,3}$ levels by 10_0^0 and 12_2^0 is more pronounced in the case of the *6s6f* $^3F_{2,3}$ terms, owing to their closer proximity to the perturbing terms. This probably explains the larger difference between the two values of $a' + a''$ for the *6s6f* configuration.

Calculation of $g(I)$ Values

Formulas have been developed by a number of authors (5, 10) for the purpose of calculating from the separation factors the ratio of the magnetic to the mechanical moment of the nucleus, $g(I)$. The lack of agreement between the values of $g(I)$ derived from different terms of the same spectrum is in

some cases very pronounced, even when the relativity correction has been applied. The remaining discrepancies can usually be attributed to perturbation effects. As the h.f.s. separation factors for a large number of Tl II terms are known with considerable accuracy, it is of interest to compare the $g(l)$ values derived from these separation factors. Racah (10) has already done this for a few terms of Tl II, and his method is used here. For a two valence electron spectrum in which one electron is in an s state and the other is in a non- s state, Racah's Equations (11) and (12) may be expressed in the following form:

For $J = l + 1$

$$g(I) = \frac{A.J. \ 1838}{\left(\frac{8\pi}{3} \psi_s^2(o) \frac{\mu_o^2}{hc} K + \frac{4l(l+1)}{2l+3} \frac{\mu_o^2}{hc} \frac{\bar{1}}{r_l^3} \right)} \quad (1)$$

For $J = l - 1$

$$g(I) = \frac{A.J. \ 1838}{\left(-\frac{l-1}{l} \frac{8\pi}{3} \psi_s^2(o) \frac{\mu_o^2}{hc} K + \frac{4(l^2-1)}{2l-1} \frac{\mu_o^2}{hc} \frac{\bar{1}}{r_l^3} \right)} \quad (2)$$

where

A is the separation factor

l is the azimuthal quantum number of the non- s electron

J is the inner quantum number of the term

$\psi_s(o)$ is the value of the eigenfunction of the s electron at origin

μ_o is the Bohr magneton

r_l is the radius vector of the orbit of the non- s electron

K is the relativity correction applied only to the s electron.

Since the coupling is intermediate, the separation factors for the singlet and triplet terms for $J = l$ can be used only as a sum, and Racah's Equation (14) becomes:

For $J = l$

$$g(I) = \frac{(A + A') J. \ 1838}{\left(\frac{1}{l+1} \frac{8\pi}{3} \psi_s^2(o) \frac{\mu_o^2}{hc} K + 4l \frac{\bar{1}}{r_l^3} \right)} \quad (3)$$

where $A + A'$ is the sum of the separation factors of the two terms.

K for the $6s$ electron of Tl II is 2.31, and

$$\frac{8\pi}{3} \psi_s^2(o) \frac{\mu_o^2}{hc} K = 2340$$

$\frac{\bar{1}}{r_l^3}$ can be evaluated from fine structure data.

The results recorded in Table VI were obtained with these formulas and values.

TABLE VI
VALUES OF $g(I)$ DERIVED FROM SEPARATION FACTORS OF TI II TERMS

Term	$g(I)$	Term	$g(I)$	Term	$g(I)$
$6s6d\ ^3D_1$	2.22	$6s7d\ ^3D_1$	2.30	$6s8d\ ^3D_1$	2.41
$6s6d\ ^3D_3$	2.24	$6s7d\ ^3D_3$	2.26	$6s8d\ ^3D_3$	2.29
$6\ ^3D_2 + 6\ ^1D_2$	2.56	$7\ ^3D_2 + 7\ ^1D_2$	2.58	$8\ ^3D_2 + 8\ ^1D_2$	2.10
$6s5f\ ^3F_2$	2.34	$6s6f\ ^3F_2$	2.61	$6s7s\ ^3S_1$	†2.25
$6s5f\ ^3F_4$	2.30	$6s6f\ ^3F_4$	2.46	$6s7p\ ^3P_2$	2.16
$5\ ^3F_3 + 5\ ^1F_3$	2.17	$6\ ^3F_3 + 6\ ^1F_3$	1.82	$7\ ^3P_1 + 7\ ^1P_1$	2.77

*Calculated by Racah.

†The second term in the denominator of Equation (1) is in this case $\frac{8\pi}{3} \psi_{1s}^2(0) \frac{\mu_0^2}{hc}$, and according to Racah has the value 570.

It is observed that the $g(I)$ values obtained from the 3D_1 and 3D_3 terms are fairly consistent, and agree closely with the value derived from the $7\ ^3S_1$ term. This is to be expected since the $^3D_{1,3}$ terms and $6s7s\ ^3S_1$ are unperturbed.

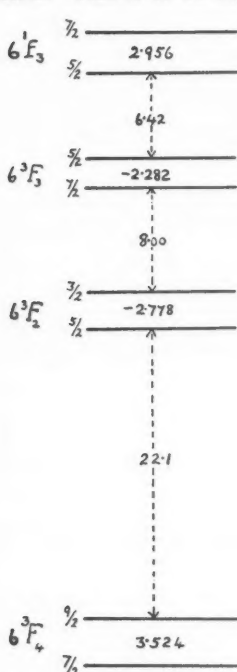


FIG. 6. Term levels of the $6s6f$ configuration ($\Delta\nu$ in cm^{-1})

The perturbation of the $6s6d\ ^1D_2$ terms by $6p^2\ ^1D_2$, the quantum defect being much above the normal for $6s7d\ ^1D_2$ and below the normal for $6s8d\ ^1D_2$. The progression of the quantum defects for the $6s6d\ ^3D_2$ terms also has a small irregularity in the neighborhood of the $6s8d\ ^3D_2$ term. The perturbation of the $6s6d\ ^1D_2$ terms by $6p^2\ ^1D_2$ would account for the deviation of the $g(I)$ values in the third row from those in the two first rows. The value from $8\ ^1D_2 + 8\ ^3D_2$ lies fairly close to the values obtained from the $6s6d\ ^3D_{1,3}$ and $6s7s\ ^3S_1$ terms. It has already been mentioned that the summation rule appears to be valid for the $6s8d$ configuration. The perturbation of $6s5f\ ^3F_{2,3}$ and $6s6f\ ^3F_{2,3}$ by 10^0 and 12^0 would cause variations in the $g(I)$ values derived from these terms. The term $6s7p\ ^1P_1$ is very strongly perturbed by 8^0_1 . This causes the large value of $g(I)$ derived from the $7\ ^3P_1 + 7\ ^1P_1$ separation factors.

The values of $g(I)$ in Table VI for the unperturbed terms are considerably smaller than those given for TI by Fermi and Segré (3), Schüler (12), and Goudsmit (5). These are 2.82, 2.94 and 3.6 respectively.

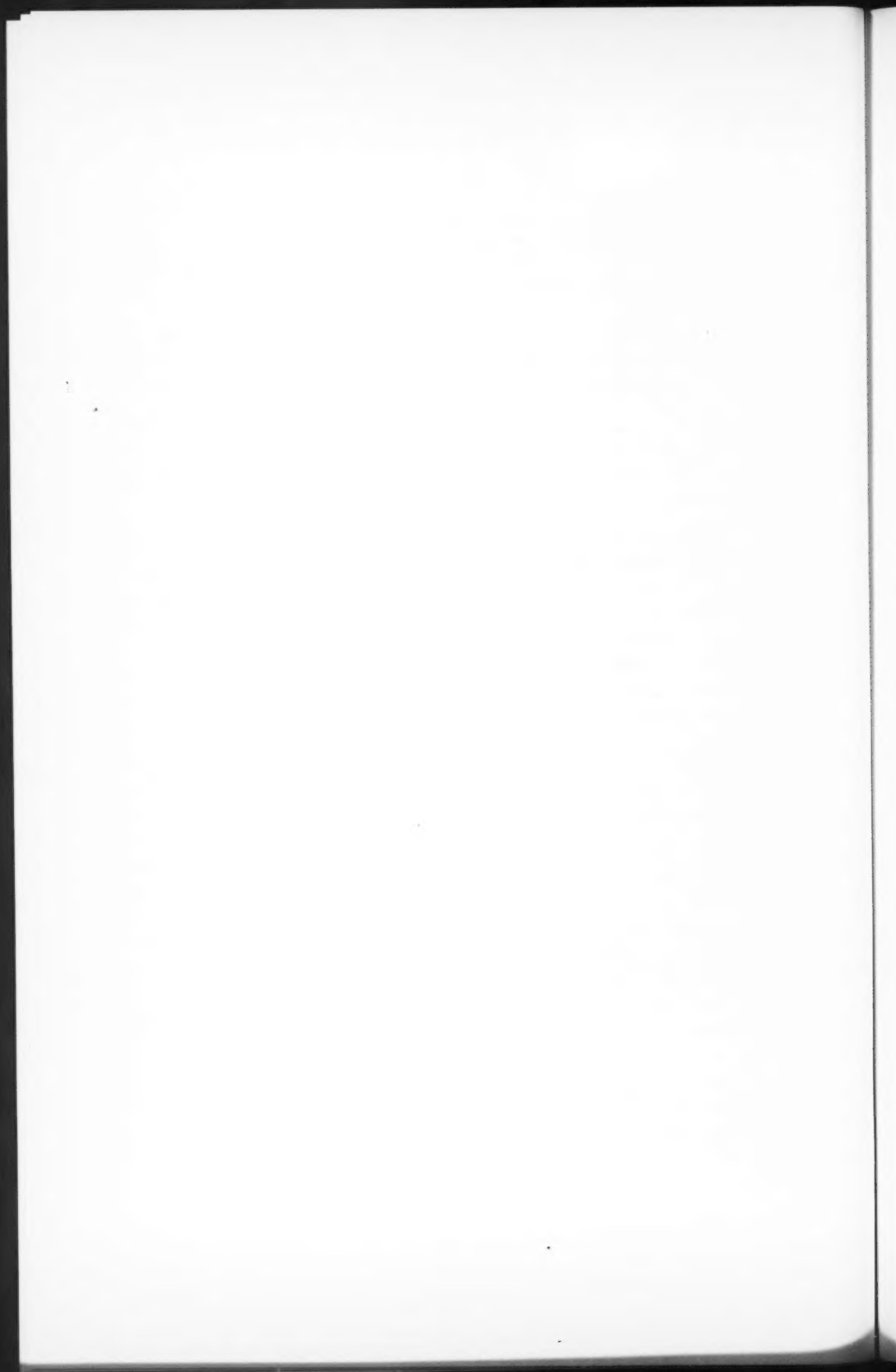
The 6s6f Terms

The terms arising from the 6s6f configuration have fine structure separations almost as small as the h.f.s. separations of the individual terms. Also the 3F_3 terms are so close together that considerable perturbation effects between them are to be expected. As this is a case of some interest, the spacing of the levels of the entire system has been carefully investigated. The results are shown in Fig. 6.

The combination of the 6s6g terms with the 6s5f terms, which lie in the region $\lambda 6167$ to $\lambda 6113$, should provide very interesting data, as it is probable that the h.f.s. of the 6s6g terms is coarser than the hyperfine structure. An attempt was made to investigate these combinations, but as they occur in a region of such low dispersion in the spectrograph there is a good deal of overlapping of the interference fringes, and no definite conclusions were arrived at. It is hoped that a further attempt with a narrower slit in the spectrograph and more intense light from the discharge tube will prove to be successful. The 6s7f $^3F_{2,3,4}$ and 6s7f 1F_3 terms should also have an interesting distribution of h.f.s. levels, which it is hoped will be revealed by a study of their combinations with the 6s6d terms.

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THE BASE-EXCHANGING PROPERTIES OF SYNTHETIC ALUMINO-SILICATE MATERIALS¹

BY J. B. FERGUSON², J. R. MUSGRAVE³ AND J. R. PATTON⁴

Abstract

The base-exchanges silver \rightleftharpoons sodium and copper \rightleftharpoons sodium have been studied over a wide range of experimental conditions. An equation of the type $\frac{x}{y} = a + bx$ was found suitable for the correlation of many results. The effects of temperature, anion, solvent and dilution upon the exchange reaction were observed.

Introduction

The base-exchange reaction is one of considerable interest to soil chemists and is also one of great industrial importance. References to the voluminous literature may be found in the reviews by Martin (9) and by Randall and Cann (11). There is now no generally acceptable quantitative theory (6, 8, 14), and the important factors that affect exchange reactions have not yet been recognized. These facts led the present writers to undertake a further study of the problem, especially since so many investigations of such reactions have been of limited scope.

Experimental

The Silver \rightleftharpoons Sodium Exchange*

The crude base-exchanging materials were Doucil, Decalso, Crystalite, Fusion Material and a base-exchanging silica gel. With the exception of the silica gel, all have been used as commercial water-softening preparations. The Fusion Material had been prepared by the fusion of the proper ingredients, with subsequent hydration. Selected grains of these substances were used. The first three were washed with distilled water until the pH of the wash water was slightly above that of the original water, and the other two were extracted with water in a Soxhlet apparatus. The silica gel was shaken with a solution of sodium chloride and then washed free of chlorides. These treatments were sufficient to ensure a uniform behavior of selected samples. The materials were analyzed by the standard method of Hillebrand (4); all the samples were decomposed by hydrochloric acid. The analyses are

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* Experimental work by Musgrave unless otherwise stated.

given in Table I. Since the water content of each material varied from day to day, it was necessary to determine either the silica or sodium content of each batch of materials before use in exchange experiments.

TABLE I
ANALYSES OF BASE-EXCHANGING MATERIALS

Material	Weight per cent				
	Na ₂ O	Al ₂ O ₃	SiO ₂	H ₂ O	Fe ₂ O ₃
1. Doucil	10.26	14.65	52.35	22.74	
2. Decalco	8.77	15.34	54.56	21.33	
3. Crystalite	7.40	11.94	59.00	21.66	
4. Fusion material	13.46	25.50	44.83	16.21	Trace
5. B.E. silica gel	2.10		78.83	19.07	Trace

NOTE—Water determined by difference.

The base-exchanging material that had passed a 100 mesh sieve was weighed into a Frazer (3) rocker tube, bottle, or flask, to which was added the calculated amount of solution. The receptacle was stoppered and shaken at a temperature that did not vary more than one degree from 25° C. The final solutions were analyzed for silver by the Volhard method, and it was assumed that the differences between the initial and final silver contents of the solutions represented the amounts of the exchange.

Several samples of each material were shaken at 25° C. with equivalent amounts of *N*/4 silver nitrate solution for periods of time ranging from one-half to as long as seven hours in some cases. Within the experimental error, the apparent equilibrium was attained in one-half hour. Additional experiments showed that the dilution of the solution from *N*/4 to *N*/10 had no appreciable effect. Musgrave assumed these experiments to be indicative of the general behavior. However Patton found that with higher percentages of silver in the solution there was an appreciable time effect, but this did not appear to be due to a normal silver⇌sodium exchange.

When Doucil was heated at 125 or 200° C. for 24 hr. and allowed to cool in air, there was no apparent change in the base-exchanging property. But when it was heated in a crucible over a blast burner flame, it sintered, and, after it had been cooled in air and reground to 100 mesh, it seemed to have lost virtually all its base-exchanging property. Experiments at 25 and 65° C. indicated no shift in the apparent equilibrium between unheated Doucil and silver nitrate solutions. The dilution of the solutions from *N*/4 to *N*/200 did not affect the amount of the exchange, nor was there any when silver acetate was substituted for silver nitrate. In these experiments, also, equivalent quantities were used. These observations are in accord with those of Rothmund and Kornfeld (12).

Several series of experiments were made in which various amounts of *N*/4 silver nitrate solution (*N*/10 in the case of the silica gel) were shaken with

various amounts of the different gel materials which contained, initially, all the sodium. A number of experiments were also made in which the initial solutions contained both silver nitrate and sodium nitrate, and the solid was Doucil. The relative amounts of the bases present initially in the solution and in the gel are given approximately in Table II. Owing to the volume limitation set by the writers' apparatus, the amount of Doucil varied from experiment to experiment.

TABLE II
THE SODIUM NITRATE-SILVER NITRATE EXPERIMENTS

Exp. series	Na Doucil	Na (Sodium nitrate, <i>N</i> /4)	Ag (Silver nitrate, <i>N</i> /4)
A II	1	0	Variable (0.2-5)
A III	1	(0.1-49)	1
B III	1	(0.5-100)	5
C III	1	4	(1-20)
D III	(0.5-8)	2	5

Silver Doucil, in which 94.2% of the sodium was replaced with silver, was prepared by shaking 100 mesh sodium Doucil with solutions of silver nitrate until no more silver was taken up by the gel. Especial care must be taken if white products are to be obtained, and therefore this work was done in a dark room. Part of this silver Doucil was reconverted back to sodium Doucil that contained 90.7% of the original sodium content by shaking with solutions of sodium nitrate. This reconverted sodium Doucil was treated with silver nitrate solutions in a series of base-exchange experiments, and a similar series, but with sodium nitrate solutions, was made with the silver Doucil. The silver-containing Doucils were decomposed with nitric acid and analyzed. Check analyses on sodium Doucil were satisfactory.

Results*

In the absence of any satisfactory quantitative theory there is no definite guidance regarding the choice of variables, or the best method of expressing these variables for the correlation of results. The writers' procedure was similar to that used by Ramann and Spengel (10). The milli-equivalents of silver in the final gel have been plotted against the equivalent percentage of silver in the final solution, that is, E_1' against P . In order to have a common basis for comparison, the unit of gel that initially contained 3.680 milli-equivalents of sodium was chosen.

The results obtained with various materials, which contained initially all the sodium, and *N*/4 silver nitrate solutions. at 25° C. are indicated in Fig. 1. Two curves are given for Doucil. Patton found that the material selected by him differed somewhat in properties from that selected by Musgrave. Later experiments seemed to show that the differences were chiefly in capacity, and Patton was able to obtain large differences by a suitable selection of

* Experiments usually done in duplicate or triplicate.

material. Since selected grains were used in these and other experiments, the writers' results should not be used for a comparison of the properties of the commercial materials. Once the water content of a type of material was checked, the composition of a sample was sufficiently uniform for experimentation, as later results on dilution will show.

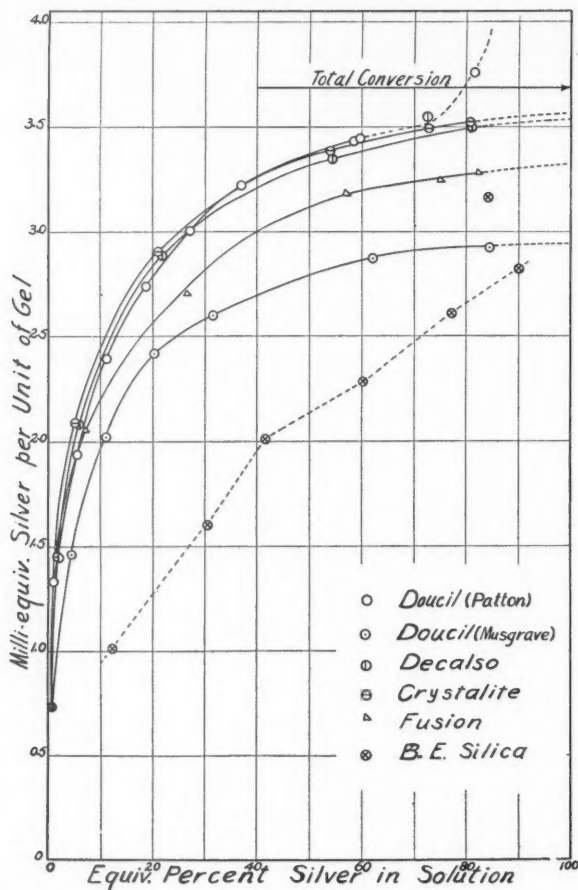


FIG. 1. The silver-sodium exchange with various materials at 25° C.

The high points at the upper end of Patton's curve for Doucil are similar to some obtained in the copper-sodium exchange, and appear to be due to additional reactions.

The results with B.E. silica gel are the least concordant and were obtained with *N*/10 silver nitrate solution. They are chiefly of interest since they confirm the observation of Biesalski (2) that a gel which contains no alumina

will act as an efficient base-exchange material. This exchange curve differs somewhat in shape from the other curves, so that the type of reaction appears to be somewhat different in character. However it must be remembered that the use of a unit containing 3.680 milli-equivalents causes the experimental errors to be greatly magnified in this case, since the amount of gel that could be used in an experiment was limited and the initial gel contained so little sodium.

The results for silver Doucil (94.2%) and sodium nitrate solutions ($N/4$), the results for the mixed solution series (Table II), and the results for the reconverted sodium Doucil and silver nitrate solutions ($N/4$), all at 25°C ., are indicated in Fig. 2. The reconverted sodium Doucil contained some silver,

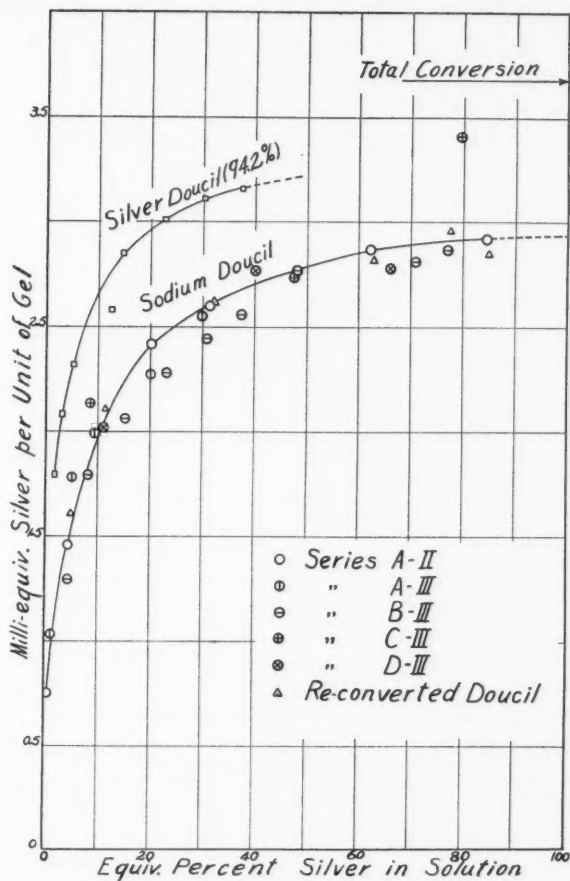


FIG. 2. The silver-sodium exchange with silver Doucil and sodium nitrate, $N/4$, and with sodium Doucils and various solutions, all $N/4$, at 25°C .

and it is a question whether this should be included in the calculation of the gel unit. But the results are far removed from the curve for silver Doucil and approximate the original curve for sodium Doucil in both cases. This fact proves that the discrepancy between the two curves is not caused by the initial selection of different kinds of Doucil grains.

The agreement between the original Doucil curve and the results for the mixed solution series is not as good as might be desired, but the range of experimental conditions was very great. In a somewhat similar series on the calcium-sodium exchange a better agreement was obtained; Vanselow (13) and Hisschemöller (5) have noted that hysteresis effects were more marked in uni-univalent exchange reactions. Except for the high point in Series C, these results suggest that an equilibrium was approximately attained, and that the final state of the system was in each case fixed by the equivalent percentage of silver in the final solution. Evidently it must be considered that silver Doucil is a material different from sodium Doucil, and the chief difference is probably one of capacity. If this be true, it would appear that the character of the gel does not progressively change in this respect as the cationic content changes. In long continued experiments, the change does occur, as for example, when silver Doucil was prepared or when it was reconverted to sodium Doucil. The above-mentioned high point in Series C might be due to the gel having changed to the silver Doucil type, a change induced by the high silver content of the gel. This question of the available capacity of a gel will be discussed later.

There is here no definite evidence that "working" a gel changes its base-exchanging properties, although Hisschemöller (5) has reported this to be the case. Owing to the fact that silver Doucil was affected by light, it was impossible to investigate this point further.

The curves in Figs. 1 and 2 suggest that the results might be expressed by the equation

$$\frac{P}{E_1'} = a + bP, \quad (1)$$

in which P is the equivalent percentage of silver in the solution, E_1' the milliequivalents of silver in the gel, and a and b are constants. Fig. 3 indicates that a linear relation of this nature holds over wide ranges of the solution percentages. In making this test, the point at 12.6% for silver Doucil, the point at 72.4% for Decalso, and the two upper points on Patton's curve for Doucil were not considered. Two straight lines include the whole set of results with Decalso, but in general the equation does not hold as well at the lower solution percentages.

If the gel capacity $E_1' + E_2'$, be considered constant, Equation (1) may be written

$$\frac{E_1'}{E_1' + E_2'} = \frac{cP}{1 + dP}, \quad (2)$$

in which c and d are constants. It may also be written

$$\left(\frac{E_2'}{E_1'}\right)_{gel} - m = n \left(\frac{E_2'}{E_1'}\right)_{soln.} \quad (3)$$

in which m and n are also constants. Equation (2) may be compared with the Langmuir equation (7)

$$\theta_1 = \frac{\alpha\mu}{1 + \beta\mu}, \quad (4)$$

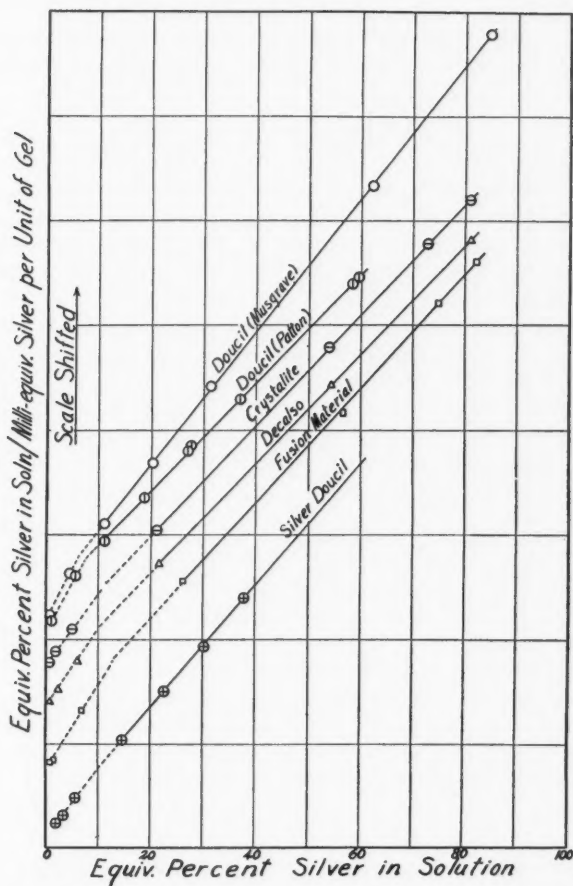


FIG. 3. The silver-sodium exchange results at 25° C. to illustrate the use of the equation $\frac{P}{E_1} = a + bP$.

in which θ_1 is the fraction of the surface covered, and μ the rate at which the molecules of gas strike the plane surface. If one could assume that the parts of a gel not covered by silver cations but by sodium cations were empty in so far as the former cations were concerned, the first terms of Equations (2) and (4) would have similar meanings. Langmuir assumed that μ was pro-

portional to the gas pressure. In the present case it might be assumed that the effective rate at which the silver cations strike the gel is proportional to the equivalent fraction of silver in the final solution, *i.e.*, to the equivalent percentage. However the writers do not regard this as a theoretical basis for their equation.

Equation (3) is of interest in that it gives a relation between the cationic ratios for the gel and for the solution, although the actual capacity of the gel is unknown.

The Copper \rightleftharpoons Sodium Exchange*

Experimental

In these experiments the procedure was essentially the one previously described. The solid material was that which passed a 100 mesh sieve but was retained on one of 200 mesh. Samples were shaken for periods of time ranging from 30 to 90 min. The final solutions were analyzed for copper by an iodometric method (Musgrave), or by weighing the copper deposited upon a platinum electrode (Patton). The copper in the alcoholic solutions was determined after the removal of the alcohol by evaporation. Alumina was determined as the oxide, or by the use of 8-hydroxyquinoline. When necessary, the solutions were evaporated to a small volume before analysis, and careful blank determinations were made. A certain duplication of the work of Musgrave was necessary in order that results on strictly comparable materials would be obtained.

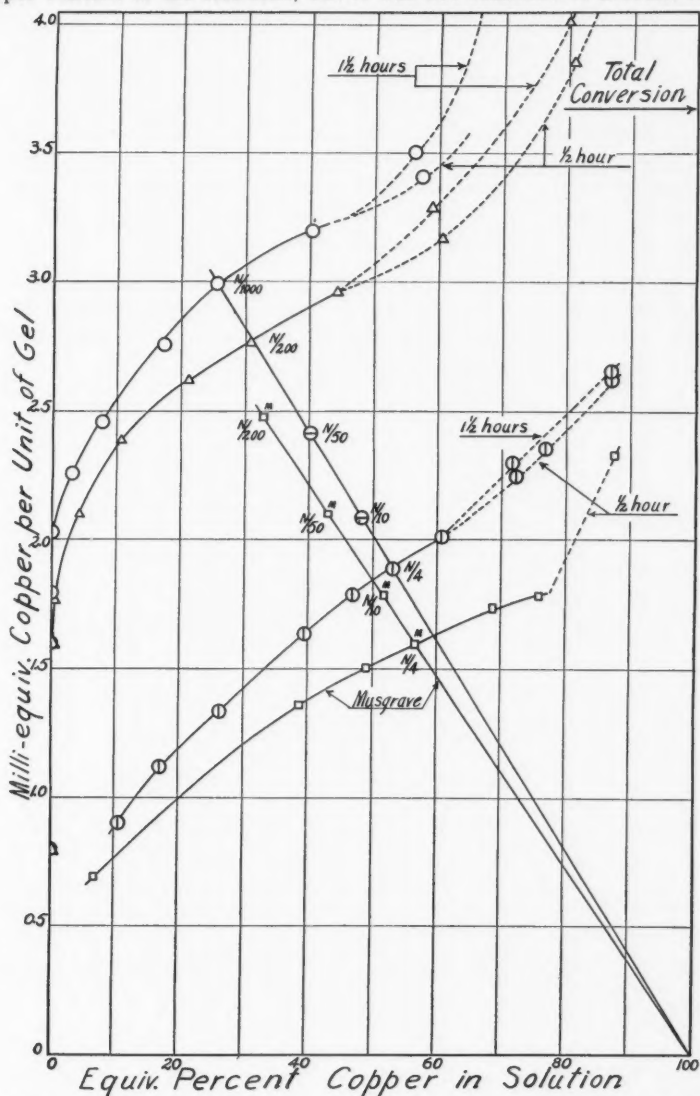
Results

Several series of results are indicated in Fig. 4. These include a curve for $N/4$ cupric nitrate and Doucil at 25° C. by Musgrave, and similar curves with $N/4$, $N/200$ and $N/1000$ cupric nitrate at 21° C. by Patton. Additional points at other normalities were also obtained in experiments in which the initial ratios of copper in the solution to sodium in the gel were maintained constant for each series. Those of Musgrave are marked (*M*). The points for each series should fall on a straight line, the position of which is fixed by the value of the constant initial ratio. The lines given in Figs. 4 and 6 for the dilution series indicate that the ratios could be maintained constant for a series with Doucil if sufficient care were taken to allow for the variable water content.

The amount of exchange varies with the normality of the initial solution. There appears to be a difference in exchange capacity between the samples of Doucil used by the two men, but the dilution effects are essentially of the same character in both cases. At high equivalent percentages for the solution a time effect was noted by Patton, and the results are abnormally high for the longer experiments. The points obtained with $N/200$ and $N/1000$ solutions could not all be plotted, since they were well above the total conversion value of 3.680, and one point was obtained at 5.1 milli-equivalents. Patton also found two somewhat similar high points in his work on the previous exchange reaction, although the effect was not so marked. An attempt was

* Experimental results by Patton unless otherwise noted.

made to determine the cause of these high points. The final copper nitrate solutions were analyzed for silica and for alumina. There was no doubt that the extent of solution of the gel material increased with increase in the copper content of the solutions, but it was not sufficient to account for the



points. The writers were unable to prove that alumina was being replaced by copper, since the alumina analyses were not very satisfactory. Such an exchange would be in accord with the observations of Austerweil (1). There can be little doubt that, in this range of solution percentages, reactions other than the normal exchange reaction also occur, and they are slower than the latter.

In certain cases, all the copper was removed from the solutions by the gel, and the removal was so complete that the copper in the solutions could not be determined quantitatively nor detected by the potassium ferrocyanide test. A faint test was obtained with rubeanic acid. For the tests, the solutions were reduced in volume from 800 to 50 cc. The solution corresponding to the upper point on the $N/1000$ curve on the zero percentage axis did give a test for copper, but the amount was too small to determine.

The writers tested their equation by plotting the various results, omitting the abnormal ones at high solution percentages. The equation fits best the results obtained with $N/1000$ solutions as given in Fig. 5. Even with $N/200$

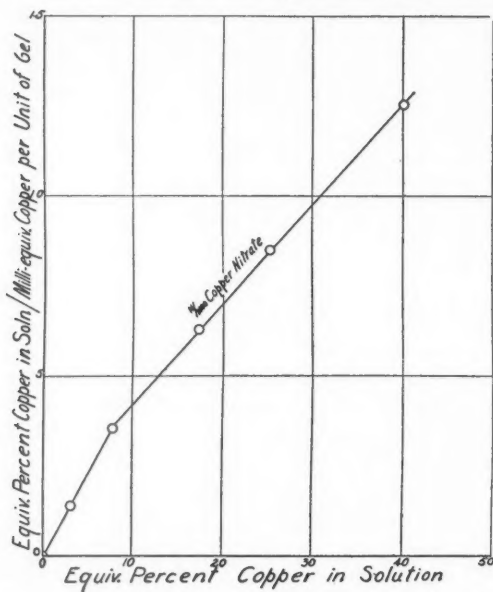


FIG. 5. The copper-sodium exchange results at $N/1000$ to illustrate the use of the equation $\frac{P}{E_1} = a + bP$.

solutions, the agreement is somewhat poorer, and it seems likely that the equation may be useful only for results at great dilution in exchanges in which dilution effects are present.

Certain dilution results obtained by Musgrave are given in Fig. 6. Had the percentage scale not been shifted, the lines would coincide. The positions of the points is further proof of the uniformity of these Doucil samples.

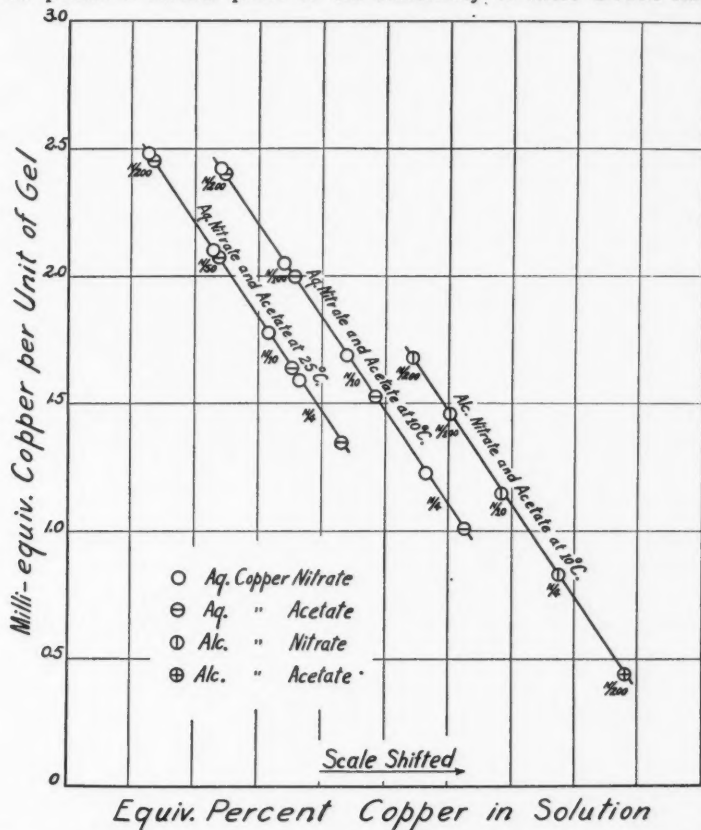


FIG. 6. The copper-sodium exchange results to show temperature, anion, solvent and dilution effects.

Anion, temperature, and solvent effects are indicated. The first two become minimized at great dilution. The writers have also observed temperature and dilution effects in the calcium-sodium exchange, so that these are not peculiar to the copper-sodium exchange.

General Discussion

The results that have been presented are hardly sufficient to provide an answer to several questions that they raise. They suggest that the writers' equation may be suitable for the correlation of many exchange results. In the copper-sodium exchange, various factors have been observed to markedly

affect the reaction. Should this prove common to other uni-divalent exchanges, the value of many comparisons of the ability of different cations to exchange would seem open to question. Results obtained at great dilution seem to be most suitable for this purpose.

The capacity of a gel for an exchange is an important question and one not easy to solve. There are many observations cited in the literature, and especially those on the difficulties experienced in the preparation of completely exchanged gels, which would lead to the belief that in many cases the capacity of a gel varies with the particular exchange reaction. This question will be further discussed at a later date, but the writers believe that the penetration of a gel by a cation is dependent on the experimental conditions, and hence its available capacity is similarly dependent. There is no certainty that the capacity remains constant over the whole range of solution percentages, and this may be the reason for the poorer agreement found between the writers' equation and results obtained at the lower solution percentages. The total removal of copper from solution in some cases would seem to favor this view.

In a later paper, the results obtained on the calcium-sodium and other exchange reactions will be presented, and the discussion continued.

Acknowledgments

Base-exchange materials were obtained from the following sources, and for these the writers wish to express their thanks:— The Permutite Co.; Zeodur, Decalso and Fusion Material: The American Doucil Co.; Doucil and B.E. Silica Gel: The International Filter Co.; Crystalite: The Silica Gel Corporation; Commercial Silica Gel.

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CONTRIBUTION À L'ÉTUDE DE LA POLYMERISATION

II. PROPRIÉTÉS, MÉCANISME DE FORMATION ET CONSTITUTION DES DISTYRÈNES ET DES POLYSTYRÈNES¹PAR J. RISI² et D. GAUVIN³

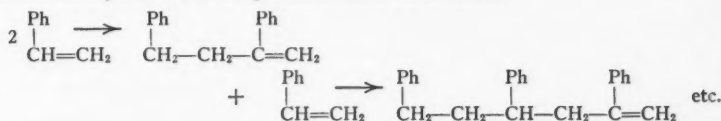
Résumé

Les auteurs prouvent que le distyrène de Fittig-Erdmann contient 30% d'un isomère saturé. Ils obtiennent le même distyrène par chauffage du styrène avec de l'acide sulfurique dilué (rendement, 65%). Par traitement avec le tétrachlorure d'étain, ce distyrène donne 50% de polymère et 50% de dimère presque entièrement saturé. Le distyrène de Stoermer-Kootz est un corps saturé, et les auteurs lui donnent la formule d'un 1-méthyl-3-phényl-hydrindène. Le di- et le tristyrene de Staudinger-Steinbofer se polymérisent par la chaleur à un degré plus élevé que le distyrène de Fittig-Erdmann; leur distyrène se polymérise totalement par le tétrachlorure d'étain et en grande partie par chauffage avec l'acide sulfurique dilué; avec le dernier réactif, leur tristyrene ne subit, par contre, ni polymérisation ni cyclisation appréciable. La polymérisation du styrène avec le pentachlorure d'antimoine donne des polystyrènes saturés; il semble en être de même de sa polymérisation avec l'acide sulfurique concentré.

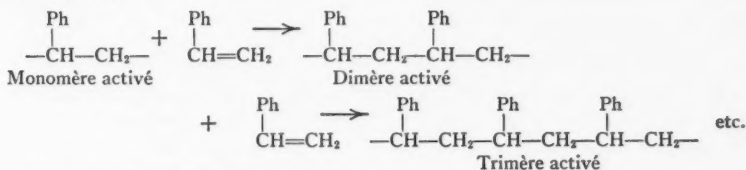
Les auteurs prouvent expérimentalement que la polymérisation du styrène se fait par un mécanisme à chaîne et ils soutiennent que ce mécanisme est différent de celui préconisé par Staudinger. L'arrêt de la polymérisation se ferait par une réaction secondaire, une cyclisation, transformant le polystyrène non saturé intermédiaire en une molécule filamentaire saturée, avec boucle terminale; cette dernière serait constituée par un anneau hydrindénique.

Introduction

Whitby (15), se basant sur les travaux de ses élèves, propose pour la formation des polystyrènes un mécanisme à étapes, suivant lequel la polymérisation du styrène se ferait par additions successives:

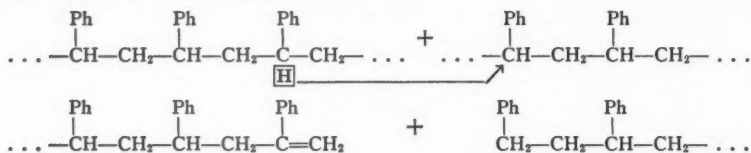


Staudinger et ses collaborateurs (9) avancent au contraire la théorie que les polystyrènes se forment par une réaction à chaîne. D'après cette théorie, appuyée par les travaux de plusieurs auteurs sur la polymérisation en général, une molécule de styrène est d'abord activée, puis d'autres molécules viennent s'ajouter à celle-ci en donnant toujours naissance à une nouvelle molécule activée:

¹ Manuscrit reçu le 20 avril, 1936.² Contribution du département de Chimie organique, Ecole Supérieure de Chimie, Université Laval, Québec.³ Professeur de Chimie organique, Université Laval, Québec.³ Chimiste de recherches, Université Laval.

Selon Staudinger, l'arrêt de la réaction à chaîne doit finalement se faire par une réaction secondaire dont la fréquence est en rapport direct avec la rapidité de la polymérisation. Afin d'obtenir des éclaircissements sur la nature de cette réaction secondaire, Staudinger et Steinhöfer (11) ont cherché à déterminer le genre des groupements finals de la chaîne polystyrénique, sans cependant arriver à un résultat positif.

La connaissance de la réaction secondaire qui met fin à la polymérisation est de haute importance. Staudinger et collaborateurs (10) ont prouvé qu'il ne peut y avoir du carbone trivalent au bout de la molécule filamentaire, et que la molécule n'est pas un anneau à nombreux membres (*vielgliedriger Ring*) (9, p. 213-217). L'auteur dit aussi que l'on pourrait envisager comme possibilité de groupement final la fermeture d'un anneau, analogue à celle observée par Bergmann dans la dimérisation de l'*as*-diphényl-éthylène (2) et de l' α -méthyl-styrène (1). Il est cependant le plus vraisemblable, dit-il (11, p. 42), d'accepter comme groupe final de la molécule filamentaire polystyrénique une double liaison, qui se formerait par migration d'hydrogène d'une chaîne à l'autre de la façon suivante:



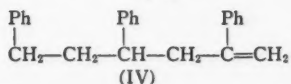
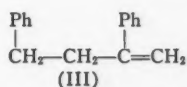
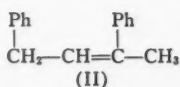
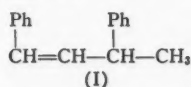
Dans un travail précédent (6), nous avons démontré que les polyindènes sont un mélange de polymère-homologues saturés et nous avions préconisé qu'ils se forment par une réaction à chaîne avec enchaînement condensant. L'arrêt de la polymérisation serait dû à une réaction secondaire: le produit intermédiaire non saturé subirait une cyclisation en donnant comme produit final une molécule filamentaire saturée avec boucle terminale. Nous avons basé cette conception principalement sur la transposition du diindène non saturé en isomère saturé (*truxane*) par simple chauffage. A la suite de ce travail, nous avons étendu notre étude aux polystyrènes et plus particulièrement aux premiers termes de cette série, espérant ainsi obtenir d'autres éclaircissements sur les processus élémentaires de la polymérisation.

Partie théorique

PRÉPARATION DES DISTYRÈNES ET DU TRISTYRÈNE

La littérature mentionne trois distyrènes non saturés. Le distyrène I, préparé d'abord par Erlenmeyer (3), fut étudié en détail par Fittig et Erdmann (4); sa constitution a été établie plus tard par Stobbe et Posnjak (12), puis confirmée par Stoermer et Kootz (13). Les derniers auteurs décrivent un autre distyrène II, obtenu par transposition du distyrène I avec de l'acide sulfurique. Staudinger et Steinhöfer (11) ont finalement trouvé un

distyrène III dans les produits de crackage des polystyrènes, ainsi qu'un tristyène IV.



Nous avons préparé ces quatre hydrocarbures afin de pouvoir comparer leurs propriétés. De plus, nous avons fait du distyrène I un corps très facilement accessible: on l'obtient avec un rendement de 65% par chauffage du styrène pendant huit heures avec cinq fois son poids d'acide sulfurique concentré préalablement dilué avec 1½ volume d'eau. Par contre, le chauffage du styrène avec de l'acide chlorhydrique donne un rendement beaucoup plus faible.

POLYMÉRISATION CATALYTIQUE DU STYRÈNE ET DES DISTYRÈNES

1. Polymérisation du styrène avec le pentachlorure d'antimoine

Par polymérisation du styrène en solution benzénique avec le pentachlorure d'antimoine, pendant quelques jours, à température ordinaire et à l'obscurité, on obtient un produit résineux qui donne, par précipitation fractionnée, deux polystyrènes, l'un de P.M. 636 et de L. 60°C., l'autre de P.M. 1335 et de L. 90-92°C. (L = point de liquéfaction). Ces deux polystyrènes inférieurs sont saturés (voir tableau I).

2. Polymérisation du styrène avec l'acide sulfurique

Le styrène, polymérisé selon la méthode décrite par Staudinger et Steinhöfer (11, p. 53), conduit à un produit collant de P.M. 433. Nous avons constaté que ce produit contient 10-15% de distyrène non saturé, qui est la cause de son aspect gras. Après la séparation du distyrène, le polystyrène restant forme une résine pulvérisable et donne par fractionnement des poudres de P.M. 827, 566 et de L. 70-72°, 53-55°C. respectivement. Ces polystyrènes inférieurs semblent également saturés (voir tableau I).

3. Polymérisation des distyrènes avec le tétrachlorure d'étain

Le distyrène I de Fittig-Erdmann, contenant 70% de dimère non saturé (voir tableau I), traité par le tétrachlorure d'étain dans les conditions décrites par Bergmann (1, p. 1499), donne 50% de polymère et 50% d'un distyrène presque entièrement saturé. Le même résultat est obtenu avec notre distyrène provenant du styrène. Il y a donc eu, dans les deux cas, polymérisation (50%) et cyclisation (15-20%). Ces résultats sont analogues à ceux obtenus par Bergmann avec le dimère non saturé de l' α -méthyl-styrène.

Par contre, le distyrène II de Stoermer n'est aucunement attaqué par le tétrachlorure d'étain, ce qui nous laisse croire que ce composé est plutôt saturé (voir aussi tableau I). Enfin, le distyrène III de Staudinger polymérise totalement dans les mêmes conditions.

ESSAIS DE CYCLISATION DES DISTYRÈNES ET DU TRISTYRÈNE

1. *Par la chaleur*

Le distyrène I de Fittig-Erdmann, chauffé à 210-215°C. pendant quatre jours en tube scellé à l'obscurité, donne seulement 10% d'un polymère, tandis qu'on récupère 90% du dimère dont le degré de saturation n'est que très légèrement diminué. En soumettant le distyrène III de Staudinger au même traitement, on obtient par contre 50% de polymère; le tristyrène IV en donne même 55%. La faible diminution du degré de saturation du distyrène III et du tristyrène IV récupérés (voir tableau I) prouve que la chaleur ne provoque pas de cyclisation appréciable de ces hydrocarbures.

Les résultats précédents montrent que le di- et le tri-styrène obtenus par crackage des polystyrènes subissent plus facilement la thermopolymérisation que le distyrène de Fittig-Erdmann. Nous avons noté avec surprise que la quantité de polymère formée est même plus considérable dans le cas du tristyrène IV, alors que, à priori, le distyrène III devrait polymériser à un degré plus élevé. Ce fait indique nettement que ces deux substances ne subissent pas de polymérisation individuelle et qu'elles ne produisent des polystyrènes qu'après dédoublement préalable en monomère. Cette considération est expérimentalement confirmée par la présence de 8% environ de distyrène associé au tristyrène récupéré après le chauffage et que nous avons pu séparer par distillation.

2. *Par l'acide sulfurique*

Le distyrène I de Fittig-Erdmann (4) se forme par chauffage de l'acide cinnamique avec de l'acide sulfurique dilué (1:1½) pendant sept à huit heures. Ce distyrène est fluorescent et donne un dibromure par addition. Par plus long chauffage dans les mêmes conditions, Stoermer et Kootz (13) ont obtenu graduellement une série de produits dont la fluorescence diminue, mais qui substituent le brome de plus en plus. Finalement, après 72 h. de chauffage, ils ont obtenu un distyrène non fluorescent, qui ne donne plus de dibromure défini, qui substitue fortement le brome et auquel ils attribuent la formule II en se basant principalement sur les produits de l'ozonisation. Ce changement graduel des propriétés nous intriguait fort et nous avons voulu contrôler le degré de saturation des produits formés.

Dans la préparation du distyrène par la méthode décrite par Fittig-Erdmann (4, p. 180), nous avons obtenu, après huit heures de chauffage, un produit fluorescent qui contient 70% de l'hydrocarbure non saturé I (voir tableau I); après 36 h. de chauffage, le produit, moins fluorescent, ne contient plus que 50% du distyrène I. Le reste est sans doute constitué par un isomère saturé. Afin de le prouver de façon indubitable, nous avons chauffé du distyrène I, préparé selon Fittig-Erdmann, avec de l'acide sulfurique dilué (1:1) pendant 40 h.; le produit non fluorescent obtenu est identique au produit final de Stoermer et Kootz, mais la bromuration démontre qu'il s'agit d'un distyrène saturé (100%).

Quand on chauffe le distyrène III dans les mêmes conditions pendant 36 h., il y a polymérisation presque complète, accompagnée de carbonisation, et on ne récupère que 10% de distyrène très impur. Le tristyrene IV, par chauffage dans les mêmes conditions, ne subit au contraire qu'une faible polymérisation (10%) et le degré de saturation du tristyrene récupéré n'est que légèrement augmenté.

ABSORPTION DE BROME

Nous avons soumis plusieurs produits de polymérisation du styrène à la bromuration d'après McIlhiney (5), dans le but de déterminer leur degré de saturation. Nous tenons à remarquer que cette bromuration est une excellente méthode pour la recherche des doubles liaisons, spécialement dans le cas de séries polymère-homologues. Pour obtenir des résultats concluants, il faut cependant observer certaines précautions sur lesquelles la littérature n'insiste pas suffisamment. Ainsi, il est très important de conserver les prises à l'obscurité jusqu'après l'addition de l'iodure de potassium, de se servir de tétrachlorure de carbone absolument anhydre et auparavant purifié par le brome et de ne mettre en opération que des petits volumes de solution.

Le tableau I permet les conclusions suivantes:

Le distyrène de Fittig-Erdmann, jusqu'ici considéré comme un corps pur, est un mélange de deux isomères contenant environ 70% du distyrène non saturé I. La proportion de l'isomère saturé n'augmente pas de façon notable par chauffage à 210-215°C. pendant quatre jours. Quand on prolonge l'action de l'acide sulfurique dans la préparation du distyrène de Fittig-Erdmann à 36 h., on obtient un mélange à parties égales d'isomères saturé et non saturé. Le distyrène de Fittig-Erdmann, chauffé pendant 40 h. avec de l'acide sulfurique 1:1, n'a cependant pas la formule II attribuée par Stoermer et Kootz, car il est saturé (100%). Il n'y a donc pas eu migration de la double liaison de la position 1, 2 à la position 2, 3, mais bien transposition en un isomère saturé par cyclisation. Le dimère récupéré dans le traitement du distyrène de Fittig-Erdmann par le tétrachlorure d'étain est aussi en grande partie saturé (90%).

Notre distyrène obtenu par chauffage du styrène avec de l'acide sulfurique est également un mélange, contenant un peu plus de l'isomère saturé que le distyrène de Fittig-Erdmann; avec l'acide chlorhydrique, par contre, la proportion de l'hydrocarbure saturé est plus faible. Par traitement de notre distyrène avec le tétrachlorure d'étain, la partie non polymérisée récupérée est presque totalement constituée par un isomère saturé (97%).

Notre préparation du distyrène pyrolytique III de Staudinger contient très peu d'hydrocarbure saturé (7%), tandis que celle du tristyrene, également obtenu par pyrolyse, en contient environ 25%. Déjà Staudinger (11, p. 48 et 49) avait trouvé que ces hydrocarbures n'étaient pas entièrement non saturés. Le distyrène III, par chauffage à 210-215°C. pendant quatre jours, subit une légère transformation, tandis que le tristyrene IV n'est guère changé. Ce dernier, chauffé avec de l'acide sulfurique 1:1 pendant 36 h., n'accuse à la bromuration qu'une légère augmentation du degré de saturation.

TABLEAU I
BROMURATION D'APRÈS MCLHINEY

Hydrocarbure	L., ° C.	P.M.	Poids de la substance, g.	Cc. de CCl ₄ comme solvant	Solution de CCl ₄ dans CCl ₄		Cc. de Na ₂ SO ₃ N/10, correspondant au		Brome consommé		Br additionné, atome par mol. g.	Br substitué, atome par mol. g.	Degré de substitution, %
					0.08 N, cc.	N/3, cc.	Br consommé	Br dégagé	Quantité molaire	Atomes par mol. g.			
1. Styryène	—	104	0.1634	5	—	10	23.50	0.2	162	2.02	1.94	0.09	—
2. Distyrène de Fittig-Erdmann (acide cinnamique chauffé 8 h. avec H ₂ SO ₄ , 1:1½)	—	208	0.2175	10	35	—	25.57	5.70	195	2.44	1.36	0.54	32
	—	208	0.1832	5	—	10	23.25	5.55	211	2.64	1.38	0.63	31
	—	208	0.2497	5	—	10	29.50	6.00	196	2.45	1.45	0.50	28
3. Distyrène de Fittig-Erdmann chauffé à 210-215° C. pendant 4 jours.	—	208	0.2175	10	35	—	25.17	6.60	208	2.60	1.25	0.67	37.5
	—	208	0.2363	5	—	10	30.35	7.95	214	2.67	1.27	0.70	36.5
	—	298	0.2000	5	—	10	27.15	7.65	228	2.85	1.24	0.80	38.0
4. Distyrène (acide cinnamique chauffé 36 h. avec H ₂ SO ₄ , 1:1½)	—	208	0.2071	10	35	—	24.47	7.30	196	2.45	1.00	0.72	50
	—	208	0.1944	5	—	10	29.00	9.55	248	3.10	1.06	1.02	47
	—	208	0.2076	5	—	10	30.35	10.00	243	3.04	1.03	1.00	48.5
5. Distyrène de Stoermer-Kootz (distyrène de Fittig-Erdmann chauffé 40 h. avec H ₂ SO ₄ , 1:1)	—	208	0.1950	5	—	10	23.60	12.40	201	2.50	—	1.25	100
	—	208	0.2098	5	—	10	28.50	14.45	225	2.80	—	1.40	100
	—	208	0.2260	5	—	10	21.25	11.10	156	1.95	—	0.98	100
	—	208	0.1842	5	—	10	19.30	10.30	174	2.16	—	1.08	100
6. Distyrène de Fittig-Erdmann traité par SnCl ₄	—	208	0.2737	5	—	10	18.80	8.10	114	1.43	0.20	0.61	90
7. Distyrène obtenu par chauffage du styrène avec H ₂ SO ₄ , 1:1½	—	208	0.2253	10	35	—	29.27	8.00	216	2.70	1.22	0.74	37.9
	—	208	0.1906	5	—	10	26.00	7.20	226	2.80	1.25	0.78	37.7
	—	208	0.1838	5	—	10	25.00	7.05	226	2.81	1.23	0.79	37.8
8. Distyrène précédent traité par SnCl ₄	—	208	0.1866	5	—	10	13.95	6.70	127	1.60	0.06	0.77	97
9. Distyrène obtenu par chauffage du styrène avec HCl à 23%	—	208	0.2044	5	—	10	19.80	1.90	161	2.01	1.62	0.20	19.0
	—	208	0.2129	5	—	10	20.70	2.10	162	2.02	1.61	0.20	19.5

10. Distyrène pyrolytique de S Saudinger	—	208	0-1717	5	—	10	19-65	4-40	190	2-37	1-85	0-26	7-5
	—	208	0-2034	5	—	10	24-50	3-15	200	2-50	1-86	0-32	7-0
	—	208	0-3214	10	—	25	41-60	6-43	215	2-68	1-85	0-42	7-5
11. Distyrène pyrolytique chauffé pendant 4 jours à 210-215° C.	—	208	0-1996	5	—	10	18-75	3-80	156	1-95	1-56	0-20	22
	—	208	0-1652	5	—	10	15-90	1-60	160	2-00	1-60	0-20	20
12. Tristyrène pyrolytique de S Saudinger	—	288	0-2040	5	—	10	14-75	4-10	166	2-07	1-51	0-28	24-5
	—	288	0-1634	5	—	10	11-05	1-27	156	1-95	1-50	0-22	25
	—	292	0-2115	5	—	10	15-10	2-30	166	2-07	1-45	0-31	27-5
	—	292	0-1838	5	—	10	13-45	2-15	171	2-14	1-45	0-34	27-5
13. Tristyrène pyrolytique chauffé pendant 4 jours à 210-215° C.	—	288	0-2477	10	—	25	28-95	8-20	269	3-36	1-46	0-95	27
	—	288	0-2106	5	—	10	17-60	3-70	192	2-40	1-40	0-50	30
14. Tristyrène pyrolytique chauffé 34 h. avec H ₂ SO ₄ 1:1	—	288	0-2160	5	—	10	15-50	3-25	165	2-06	1-20	0-43	40
	—	288	0-2341	5	—	10	16-40	3-20	161	2-01	1-23	0-39	38-5
15. Polystyrène catalytique avec le pentachlorure d'antimoine	90-92	1335	0-2500	10	35	—	4-70	2-30	200	2-50	0-05	1-23	98
	90-92	1335	0-3984	10	—	25	4-55	2-30	122	1-53	—	0-77	100
	90-92	1335	0-3376	10	—	25	4-85	2-50	153	1-91	—	0-96	100
	90-92	1335	0-2373	5	—	10	0-45	0-22	20	0-25	—	0-13	100
	60	636	0-3630	10	—	25	6-60	3-70	93	1-16	—	0-58	100
16. Polystyrène catalytique avec H ₂ SO ₄ conc. (a) Produit collant	—	433	0-5620	10	—	25	19-55	8-20	120	1-50	0-24	0-63	88
	—	433	0-5110	5	—	10	4-70	1-50	32	0-40	0-15	0-13	92
(b) Après fractionnement	70-72	827	0-2516	10	—	25	2-60	1-10	68	0-85	0-13	0-36	95-5
	70-72	827	0-5166	10	—	25	9-05	4-35	116	1-45	0-05	0-70	97-5
	70-72	827	0-1780	5	—	10	1-30	0-70	48	0-60	—	0-30	100
	53-55	566	0-3951	10	—	25	10-80	5-60	124	1-55	—	0-77	100
	53-55	566	0-4011	10	—	25	10-50	4-80	118	1-47	0-12	0-67	94
17. Polystyrène thermique	200	>10,000	0-5000	10	—	25	1-85	0-90	—	—	—	—	—
	200	>10,000	0-2522	10	25	—	0-45	0-25	—	—	—	—	—

Les polystyrènes catalytiques obtenus par action du pentachlorure d'antimoine sur le styrène sont des corps entièrement saturés, ce qui paraît aussi être le cas des polystyrènes catalytiques à l'acide sulfurique après avoir éliminé le distyrène présent dans le produit brut collant. Les résultats des polystyrènes à l'acide sulfurique sont, cependant, moins concordants, ce que nous attribuons à des difficultés expérimentales; il est, en effet, difficile d'éliminer tout le distyrène du produit collant et il se forme une émulsion rendant la titration moins précise.

Quant aux polystyrènes thermiques, il est bien difficile de tirer des conclusions, vu la faible consommation de brome des grandes molécules qui rend la distinction entre le brome additionné et substitué incertaine. Cette remarque est conforme aux constatations signalées par Watermann et Staudinger (14). Le caractère saturé des polystyrènes catalytiques, ainsi que des polyindènes thermiques et catalytiques (6), nous permet de croire que les polystyrènes thermiques sont, par analogie, également saturés.

MÉCANISME DE POLYMÉRISATION

(a) *Essai d'addition de styrène au distyrène de Fittig-Erdmann*

Nous avons chauffé dans les mêmes conditions, à 210-215°C., en tubes scellés, pendant trois jours: (1) 10 g. de styrène; (2) 10 g. de distyrène de Fittig-Erdmann; (3) un mélange de 10 g. de styrène et 10 g. de distyrène de Fittig-Erdmann.

La distillation dans le vide après chauffage a donné:

1. 10 g. de polystyrène.
2. 1 g. de polystyrène et 9 g. de distyrène récupéré.
3. 11 g. de polystyrène et 9 g. de distyrène récupéré.

Ces résultats montrent clairement que le styrène ne subit pas une polymérisation à étapes, mais bien une réaction à chaîne, puisque la réaction: styrène + distyrène = tristyrene, n'a pas lieu.

(b) *Essai d'addition du styrène au di- et au tristyrene de Staudinger*

Les substances suivantes ont été chauffées en tubes scellés à 210-215°C. pendant quatre jours:

1. 6 g. de distyrène III de Staudinger.
2. 6 g. de tristyrene IV de Staudinger.
3. un mélange de 6 g. de styrène et 6 g. de distyrène III.
4. un mélange de 6 g. de styrène et 6 g. de tristyrene IV.

Par distillation dans le vide, nous avons obtenu:

1. 3.0 g. de dimère récupéré et 3.0 g. de polystyrène.
2. 2.5 g. de tristyrene récupéré et 3.3 g. de polystyrène.
3. 2.8 g. de distyrène et 9.0 g. de polystyrène.
4. 2.0 g. de tristyrene et 9.5 g. de polystyrène.

Ces résultats font voir que les rendements en distillat récupéré et en polymère formé sont approximativement les mêmes, que les produits soient chauffés séparément ou en mélange. Le styrène ne subit donc pas de polymérisation à étapes.

Ces résultats, même plus concluants que ceux obtenus dans notre travail sur les polyindènes (6, p. 232), confirment nettement ce que nous avons dit au sujet du mécanisme de polymérisation (6, page 244).

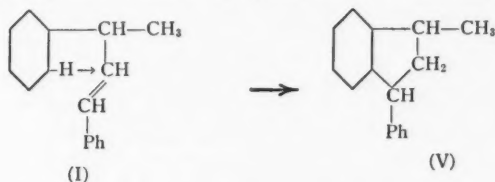
CONSTITUTION DES DI- ET POLYSTYRÈNES

(a) Constitution des distyrènes

Le distyrène de Fittig-Erdmann correspond sans doute à la formule I, prouvée par Stobbe et Posnjak, et par Stoermer et Kootz, avec la réserve cependant qu'il contient 30% d'un isomère saturé. Notre distyrène, obtenu par action de l'acide sulfurique sur le styrène, est approximativement de la même composition et démontre aussi les mêmes propriétés, de sorte que nous lui attribuons la même formule I. En effet, les deux distyrènes se polymérisent par traitement avec le tétrachlorure d'étain en raison de 50%, tandis qu'on récupère un dimère pratiquement saturé dans les deux cas.

Au di- et au tristyrene, obtenus par dédoublement pyrolytique des polystyrènes, Staudinger et Steinhöfer ont attribué, grâce à l'identification des produits d'oxydation, les formules III et IV respectivement. Par l'étude comparative des réactions avec le tétrachlorure d'étain, l'acide sulfurique dilué et la chaleur, nous avons pu constater que les distyrènes I et III se comportent très différemment. En nous basant principalement sur la très faible tendance du distyrène III et du tristyrene IV à la cyclisation, nous sommes même portés à croire que ces deux corps ne se rangent pas, comme premiers termes, dans la série polystyrénique, étant plutôt des produits typiques de crackage et non de synthèse.

Quant au distyrène de Stoermer et Kootz, celui-ci ne peut avoir la formule II, car le tétrachlorure d'étain est sans action sur cette substance et la bromuration montre qu'elle est saturée (100%). Nous lui attribuons plutôt la formule V. Ce 1-méthyl-3-phényl-hydrindène peut, en effet, se former très facilement à partir du distyrène I de Fittig-Erdmann par une simple migration d'hydrogène entraînant la cyclisation. L'isomère saturé contenu



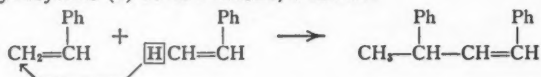
dans le distyrène de Fittig-Erdmann, préparé de la même façon que le distyrène de Stoermer-Kootz, mais par chauffage moins prolongé, correspondrait également à la formule V; il en serait de même pour l'isomère saturé contenu

dans notre distyrène formé par chauffage du styrène avec l'acide sulfurique. La formule V est analogue à celle donnée par Bergmann et collaborateurs (1) au dimère saturé de l' α -méthyl-styrène. Elle répond également aux propriétés décrites par Stoermer et Kootz, à savoir, la substitution par le brome et l'inaptitude à former des dibromures.

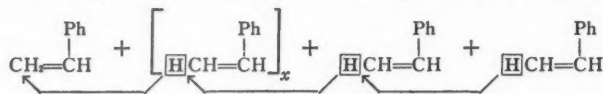
Dans un travail subséquent, nous espérons pouvoir établir définitivement la constitution de ce distyrène saturé par synthèse et oxydation.

(b) *Mécanisme de formation et constitution des polystyrènes*

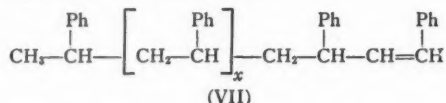
Nos observations nous permettent maintenant de formuler le mécanisme de formation et la constitution des polystyrènes. Nous avons prouvé que le distyrène I se forme directement à partir du styrène et nous admettons pour sa formation un mécanisme analogue à celui des dimères non saturés de l' α -méthyl-styrène (1) et de l'indène, à savoir:



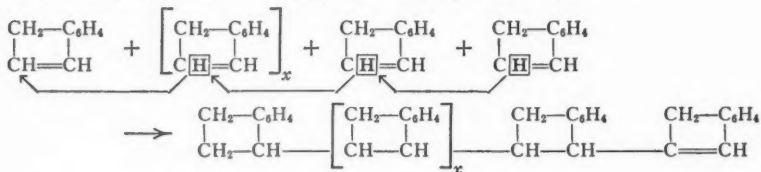
Pour les polystyrènes, nous proposons un mécanisme à chaîne analogue:



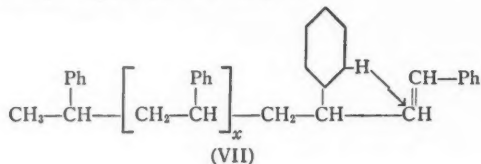
donnant ainsi un produit non saturé VII:



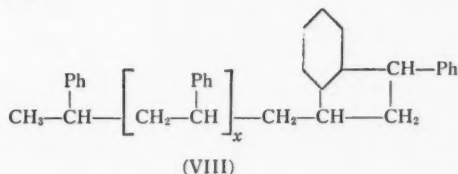
Ce mécanisme, tout en étant un mécanisme à chaîne, est différent de celui préconisé par Staudinger (11, p. 43), mais tout-à-fait analogue à celui que nous avons proposé pour les polyindènes (6, p. 242-243):



A la fin de la réaction, le produit intermédiaire VII subirait une cyclisation d'après le schéma déjà exposé pour le distyrène:

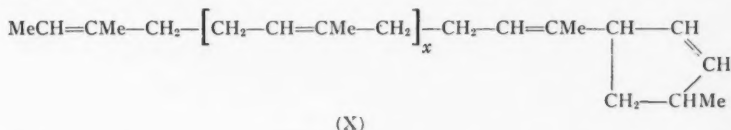


donnant ainsi VIII,



une molécule filamentaire saturée avec une boucle terminale formée par un anneau hydrindénique. Cette formule est conforme à nos résultats de bromuration des polystyrènes, ainsi qu'aux résultats négatifs obtenus par Signer (8) dans la recherche d'une double liaison dans les polystyrènes supérieurs par les spectres Raman.

Quant au caoutchouc, outre la formule d'un dérivé du cyclobutène déjà suggérée (6, p. 243, formule XV), il faut naturellement aussi considérer, par analogie à VIII, la formule X d'un dérivé du cyclopentène:



Nous ne pouvons pas nous prononcer en faveur de l'une ou de l'autre formule, quoique celle d'un dérivé cyclobuténiq ue paraît théoriquement plus probable à cause de la plus grande aptitude de l'hydrogène ternaire à la migration.

Préparations

Partie expérimentale

Le styrène fut préparé d'après la méthode de Sabetay (7). Le distyrène de Fittig-Erdmann (4), celui de Stoermer et Kootz (13), et le di- et le tri-styrène de Staudinger-Steinhofer (11) furent obtenus selon les méthodes décrites par ces auteurs, avec la modification cependant que les deux derniers produits furent préparés par polymérisation du styrène en tubes scellés à 150° C. pendant six jours et crackage subséquent à 2 mm. pendant huit heures.

Notre nouvelle méthode de préparation* du distyrène de Fittig-Erdmann consiste à faire bouillir du styrène avec un mélange de cinq parties en poids d'acide sulfurique concentré et quatre parties d'eau, pendant huit heures, en présence de pierre ponce. L'extraction et la purification du distyrène se font conformément aux méthodes décrites par Fittig-Erdmann (4). On obtient ainsi le distyrène de E. 118-120° C. à 2-3 mm, avec un rendement de 65%. On peut préparer le même distyrène par ébullition du styrène avec 10 parties d'acide chlorhydrique à 23%, pendant 10 h., mais le rendement n'est que de 25%.

* Cette préparation, ainsi que celle des différents distyrènes, a été faite en collaboration avec Monsieur Irénée Cantin, pour laquelle nous le remercions sincèrement.

ACTION DE CATALYSEURS SUR LE STYRÈNE ET LES DISTYRÈNES

(a) Polymérisation du styrène avec le pentachlorure d'antimoine

On dissout 20 g. de styrène dans 50 cc. de benzène, on y ajoute 1 cc. de pentachlorure d'antimoine et on laisse au repos pendant trois jours à température ordinaire et à l'obscurité. On dilue ensuite avec un égal volume de benzène, on lave à l'acide chlorhydrique dilué (10%), puis à l'eau, au carbonate de sodium (5%) et encore à l'eau. On filtre la solution décantée des polymères, on la sèche sur du chlorure de calcium et on précipite par l'alcool absolu. On redissout le polystyrène dans le chloroforme et par addition graduelle d'alcool absolu on obtient les fractions suivantes: Fraction I: P.M. 1335; L. 90-92°. Fraction II: P.M. 636; L. 60°.

(b) Polymérisation du styrène avec l'acide sulfurique concentré

On opère exactement selon la formule donnée par Staudinger et Steinhofer (11, p. 53). Le produit collant (P.M. 433), qui reste collant même après fractionnement par l'alcool éthylique, est purifié par distillation à 2 mm. dans laquelle on obtient 10-15% de distyrène. Le résidu forme une résine pulvérisable que l'on dissout dans l'éther et que l'on soumet à la précipitation fractionnée par l'alcool: Fraction I: P.M. 827 et L. 70-72°; Fraction II: P.M. 566 et L. 53-55°.

(c) Polymérisation des distyrènes avec le tétrachlorure d'étain

Les différents distyrènes sont traités par le tétrachlorure d'étain dans les conditions mentionnées par Bergmann (1, p. 1499) pour le dimère de l' α -méthyl-styrène; 6 g. de distyrène de Fittig-Erdmann donnent 3.0 g. de polymère et 3.0 g. de distyrène récupéré non fluorescent. Notre distyrène obtenu par chauffage du styrène avec l'acide sulfurique dilué donne les mêmes résultats. Le distyrène de Stoermer-Kootz ne réagit pas du tout dans les mêmes conditions, alors que celui de Staudinger se polymérise complètement avec fort dégagement calorifique.

Action de l'acide sulfurique dilué sur les distyrènes et le tristyrene

Quinze grammes de distyrène de Fittig-Erdmann, chauffés à l'ébullition au réfrigérant ascendant, pendant 40 h. avec 150 cc. d'acide sulfurique 1:1, donnent, après purification, 3 g. de polymère et 9.5 g. de distyrène non fluorescent et entièrement saturé.

Trois grammes de distyrène de Staudinger, traités dans les mêmes conditions pendant 36 h., se polymérisent presque complètement. En même temps, il y a forte carbonisation et on ne récupère qu'environ 10% d'un distyrène très impur.

En traitant 7 g. de tristyrene de Staudinger de la même façon, on obtient seulement 0.7 g. de polymère, la majeure partie du produit de départ étant récupérée sans changement appréciable.

Action de la chaleur sur les distyrènes et le tristyène

Le distyrène de Fittig-Erdmann, le di- et le tristyène de Staudinger, sont chauffés séparément en tubes scellés et à l'obscurité, à 210-215° C. pendant quatre jours. La distillation des produits de réaction à 2mm. donne les rendements déjà indiqués dans la partie théorique. Dans le cas du tristyène, on obtient en même temps 8% de distyrène.

Essais d'addition du styrène aux distyrènes et au tristyène.

Les quantités de produits de départ, les conditions et les rendements sont donnés en détails dans la partie théorique.

Bromurations

Les résultats obtenus par bromuration des divers hydrocarbures d'après la méthode de McIlhiney (5) figurent dans le tableau I.

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THE HOMOGENEOUS UNIMOLECULAR DECOMPOSITION OF GASEOUS ALKYL NITRITES

VII. A GENERAL DISCUSSION OF THE EFFECT OF CHEMICAL CONFIGURATION ON THE REACTION RATE¹

BY E. W. R. STEACIE², S. KATZ³, S. L. ROSENBERG⁴, AND
W. MCF. SMITH⁵

Abstract

A general discussion is given of the rate of unimolecular decomposition of an homologous series of compounds from the point of view of the Kassel theory. The experimental evidence is discussed with special reference to the decomposition of the alkyl nitrites. It is concluded that existing theories are unable to account for the progressive increase in rate as one ascends the homologous series.

Introduction

Since the discovery by Hinshelwood in 1926 that a number of organic compounds decomposed unimolecularly, the number of known unimolecular reactions has increased very rapidly. It now appears that at least the primary step in almost all organic decomposition reactions is a unimolecular change. It appears therefore that the whole question of the stability of gaseous organic substances is virtually reduced to a consideration of the magnitude of the unimolecular velocity constant, k , given by

$$k = Ae^{-E/RT}, \quad (1)$$

where A is a constant, and E is the energy of activation.

It is therefore a matter of great interest to determine the effect of chemical constitution on the magnitudes of A and E , and, in particular, to ascertain how these vary as we go from one member to the next in an homologous series.

In the past, three main series of chemical compounds have been available for the purposes of such a comparison, the aliphatic ethers (8, 10, 11), azo compounds (15-19), and certain esters and paraldehydes (1-4).

In the case of the ethers, two bonds are broken and one is formed in the reaction, the higher members decompose in a manner different from that of the lower ones, and in any case there is considerable evidence to show that the individual reactions are much more complicated than appears at first sight (27, 29, 36). The azo compounds also decompose in the main by splitting two bonds and forming one, so that the process is rather complicated for our purpose. In addition a side reaction which is almost negligible for azo-methane becomes of increasing prominence as we go up the series, and thus introduces a further complication.

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The esters and paraldehydes furnish a much more satisfactory series for comparison*. The main difficulty is that although the different reactions are here definitely comparable, nevertheless we are again dealing with reactions in which two bonds are broken and one is changed from single to double. Hence the physical significance of the activation energy is somewhat obscured.

Recently a series of investigations on the decomposition of the gaseous alkyl nitrites have been made in this laboratory (28, 30-35). It appears certain that the primary and rate-determining step in these reactions is always (20)



Hence only one bond is broken in the reaction whose rate is being measured, and it is the same bond in every case. As a result these investigations offer an ideal opportunity for a discussion of the effect of chemical constitution on the rate of reaction, and it is the object of this communication to present such a discussion. It will first be necessary to consider some aspects of the existing theory of unimolecular reactions in detail.

The Theory of Unimolecular Reactions

The modern theory of unimolecular reactions is based on the idea that activation is by collision, but that a time-lag exists between activation and reaction, most activated molecules being deactivated before they have a chance to react. As a result a stationary concentration of active molecules, calculable from the Maxwell-Boltzmann distribution, exists, and the rate of reaction is proportional to the first power of the concentration of the reacting substance. At low pressures, however, the diminished number of collisions will no longer be able to replace the activated molecules as fast as they are destroyed by reaction, their stationary concentration will fall, and hence the rate of reaction will diminish with decreasing pressure.

The theory of unimolecular reactions is mainly concerned with the interpretation of the rate-pressure curve in the region where the velocity constants begin to fall below their high pressure value. In the development of such a theory it is necessary to be more specific regarding the nature of the energy of activation. One type of theory (9) assumes that if a molecule has an energy $\geq E$ it has a definite probability of reacting, independent of its energy. This is the simplest form of theory, but it gives a rate-pressure relation which is definitely in disagreement with the facts. The other type of theory assumes that for reaction, energy must be concentrated in one particular degree of freedom, or in one vibrational bond of the molecule (12, 13, 21, 25, 26). On this basis it is obvious that the chance of getting energy $\geq E$ into one bond will be a function of the total energy of the molecule, and will increase rapidly with the excess of the energy of the molecule over E . This type of theory gives results which are in excellent agreement with the facts. There are a number of different forms of the theory, but all are essentially the same.

* For a detailed discussion see Reference (5).

We will confine our attention to that of Kassel, which is much the simplest for our purpose*.

This is based on the idea, obviously the correct one in principle, that when a sufficient amount of energy is located in one bond it will break. At high pressures we can obviously write

$$k = -\frac{1}{N} \frac{dN}{dT} = \frac{\sum_i k_i p_i e^{-\epsilon_i/KT}}{\sum_i p_i e^{-\epsilon_i/KT}}, \quad (2)$$

where N is the total number of molecules per cubic centimetre, K the Boltzmann constant, k_i is the specific velocity constant for the j th quantum state, p_i the statistical weight and ϵ_i the energy of the state. The j 's refer to activated and the i 's to non-activated states. For the type of molecule in which we are interested this expression is impossibly complicated, and we must therefore deal with a highly idealized molecule. It is therefore assumed that the oscillators are harmonic and weakly coupled, and that they all have the same frequency ν . Now suppose that a molecule in the j th state has j quanta divided among s oscillators, and that for reaction we must localize m of them in one particular oscillator. Then if the distribution is governed solely by chance we have for the number of molecules in the j th state

$$N_j = \frac{N \binom{j+s-1}{s-1} e^{-j h \nu / KT}}{(1 - e^{-h \nu / KT})^{-s}}. \quad (3)$$

And the chance that when s oscillators have j quanta a given one will have at least m is

$$\frac{j! (j-m+s-1)!}{(j-m)! (j+s-1)!}. \quad (4)$$

Hence it may be assumed that

$$k_j = A \frac{j! (j-m+s-1)!}{(j-m)! (j+s-1)!}, \quad (5)$$

where A is a proportionality factor. Hence for the rate of reaction at high pressures, k_∞ , we have

$$k_\infty = \sum_{j=m}^{\infty} k_j N_j. \quad (6)$$

Or

$$k_\infty = A (1 - e^{-h \nu / KT})^s \sum_{j=m}^{\infty} \binom{j+s-1}{s-1} \frac{j! (j-m+s-1)!}{(j-m)! (j+s-1)!} e^{-j h \nu / KT}. \quad (7)$$

On carrying out the summation this reduces to

$$k_\infty = A e^{-m h \nu / KT}. \quad (8)$$

At low pressures we have to take into account the number of collisions, etc., and for k , the rate at a pressure where we have N molecules per cubic centimetre, we get

* See especially Kassel (14, pp. 94-101).

$$k/k_{\infty} = (1 - e^{-h\nu/KT})^s \sum_{i=m}^{\infty} \frac{\binom{j-m+s-1}{j-m} e^{-(j-m)h\nu/KT}}{1 + \frac{A}{aN} \frac{(j-m+s-1)!j!}{(j-m)!(j+s-1)!}}, \quad (9)$$

where a is a collision factor, and involves the molecular diameter, σ .

In practice, from Equations (1) and (8) we obviously have $m h \nu = E/N_0$, where N_0 is Avogadro's number. Values of ν are frankly chosen to make the observed and calculated values of k/k_{∞} at various pressures coincide. They must however be plausible from the point of view of the known vibrational frequencies of the molecule. The number of effective oscillators in the molecule, s , is taken as the total number ($3n - 6$) (where n is the number of atoms in the molecule) less the number of C-H bonds, since these have a very high frequency and would almost never be thermally excited.

The Relative Rates of Reaction of Members of an Homologous Series

What we are mainly interested in is the variation in k_{∞} , the rate of reaction at high pressures, and in k/k_{∞} , the falling-off in rate at low pressures, as we ascend an homologous series. For what we might call an ideal series of homologues, we have the same bond broken in each molecule, and a constant bond strength throughout the series. Hence if we start with say, a methyl derivative, and find the value of m required to fit the experimental rate-pressure curve for a given value of s , then for the next member of the series we should have $s_{Et} = s_{Me} + 7$. Obviously if E/N_0 represents the energy required to break the bond, and the bond strength remains unaltered, then since

$$E/N_0 = m h \nu,$$

m must remain unaltered and we have $m_{Et} = m_{Me}$.

Hence it follows from Equation (8) that k_{∞} should be the same for all the members of the series, and independent of s^* , provided that the proportionality constant A does not vary. We will return to the possibility of such a variation later.

* This conclusion is at variance with that reached by Coffin from the same premises. He used Equation (4) to calculate the probability of a molecule with a given s and j having m quanta in a specified degree of freedom. He then assumed that as one ascends an homologous series s/j remains constant, but the individual values of both increase. This led to the prediction that the rate should increase with increasing molecular complexity. For idealized molecules of the type we are considering it is, of course, true that s/j_{av} is constant at constant temperature, where j_{av} is the average number of quanta per molecule. The rate, however, is not equal to k_i for some assigned value of j , but is given by

$$k_{\infty} = A \sum_{i=m}^{\infty} N_j k_i, \quad (10)$$

and there is no justification for singling out specified values of k_i for comparison. When the summation is performed we obtain the result given in Equation (8), i.e., k_{∞} is independent of s , other factors remaining the same.

This result can be obtained very simply in another way. The theory assumes statistical equilibrium giving the Maxwell-Boltzmann quota of activated molecules, i.e., that this distribution depends only on chance. It also assumes a chance distribution among the s oscillators of an individual molecule. The result is therefore, as long as we have freedom of distribution, the same as though all the oscillators in the gas were independent, and it is independent of the grouping of oscillators into molecules. The importance of s comes in only at low pressures where we have free redistribution among the s oscillators of a given molecule, but imperfect redistribution between oscillators in different molecules on account of the diminished number of collisions.

The Nitrite Decompositions

The results so far obtained for the nitrite decompositions at high pressures are:

$$\begin{aligned}
 k_{\text{methyl}} &= 1.84 \times 10^{13} e^{-36400/RT} \text{ sec.}^{-1} \\
 k_{\text{ethyl}} &= 1.39 \times 10^{14} e^{-37700/RT} \\
 k_{\text{propyl}} &= 2.75 \times 10^{14} e^{-37650/RT} \\
 k_{\text{isopropyl}} &= 1.26 \times 10^{14} e^{-37000/RT} \\
 k_{\text{butyl}} &\sim 3.02 \times 10^{14} e^{-37000/RT}
 \end{aligned}$$

The interdependence of the exponential and non-exponential factors in the above expressions masks any regularities. It is obvious that the heats of activation are identical within the experimental error, and this can be shown by replotting $\log k$ against $1/T$ for all the members of the series, and drawing lines of constant slope for all of them. If we recalculate the results for all the compounds with E equal to 37000 cal. we obtain:

Substance	A	A/A_{methyl}	Substance	A	A/A_{methyl}
Methyl	0.33×10^{14}	(1.0)	Isopropyl	1.26×10^{14}	3.8
Ethyl	0.65×10^{14}	2.0	Butyl	3.02×10^{14}	9.1
Propyl	1.35×10^{14}	4.1			

In other words, the rate approximately doubles for each added CH_2 group. This is in general agreement with Coffin's results for more complicated compounds, *i.e.*, a constant E and a slight increase in rate as one ascends an homologous series. It is noteworthy that the rates for the two isomeric propyl nitrites are identical within the experimental error.

If we make the calculations for the results with methyl nitrite at low pressures according to the Kassel theory (*i.e.*, Equation (9)), we find perfect agreement with experiment if we assume $\sigma = 3.0 \times 10^{-8}$ cm., $\nu = 910$ cm.⁻¹, $m = 14$, and $s = 12$. If ethyl nitrite behaved in an identical manner, except for the increased number of atoms to the molecule, then we should have $\nu = 910$ cm.⁻¹, $m = 14$, $s = 19$. On this basis we obtain results which are in perfect agreement with preliminary experiments with ethyl nitrite at low pressures.

The Kassel theory is therefore in excellent general agreement with the experimental results. It offers, however, no explanation of the increase in rate as we go up the series. The factors involved which might be concerned in such a change are:

(a) *The diameter and mass of the molecule, steric factors, etc.* These enter into the rate expression (Equation (9)) only in the quantity a (which is equal to $4\sqrt{\pi KT/m_0\sigma^2}$). The quantity a occurs only in the last term of the denominator, and this term is equal to zero at high pressures. Hence all these factors can have no effect on the value of the high pressure rate.

(b) *The number of oscillators in the molecule.* As we have pointed out above, the terms in s cancel out at high pressures.

(c) *The quantity j .* This is governed entirely by the Boltzmann distribution at high pressures, and can have no effect in the present discussion.

(d) *E , m , and ν .* There is evidence that in some cases bond strengths may diminish as we ascend an homologous series. It is therefore possible that E changes slightly from member to member, and that the non-exponential factor is really constant. Since we have equated $m h \nu$ to E/N_0 , this would be equivalent to a change in either m or ν . The theory is, of course, highly idealized, and hence m and ν have really only a rather hazy significance from a strict quantum point of view. If we kept ν constant, and there is some evidence that this is true in the series of azo compounds, then a change of 1 in m would correspond to a lowering of E by 2500 cal. from member to member of the series. This is far too high, an amount of 600 cal. being sufficient to account for the change. However, in view of the highly artificial character of the "quanta" involved, it is perhaps permissible to give m fractional values, and if so a change in m of about 0.25 from member to member would account for the results.

(e) *The proportionality factor A .* There is also the possibility that E remains strictly constant, as appears to be the case, and that A itself changes. A enters into the theory as the proportionality constant in Equation (5). It is a rather ill-defined measure of the number of times the energy of the molecule is redistributed per second, *i.e.*, it has the general significance of the reciprocal of a relaxation time (its dimensions being sec.^{-1}). It is possible that the ease of redistribution of energy throughout the molecule may vary, and hence A alters its magnitude as we go from compound to compound.

It is apparent that the general agreement of the results with theoretical predictions is excellent. The variations in rate from compound to compound cannot be accounted for by the existing theory, but this is not surprising in view of its highly idealized nature. These variations are, however, comparatively small both in the nitrite series and in the esters and paraldehydes, and thus even the greatly over-simplified model is only slightly incomplete. The existing theory must, however, be made very much more detailed before any quantitative attempt can be made to explain the present results.

One of the most promising lines of attack on the problem is contained in recent papers by Eyring (6) and by Rice and Gershinowitz (7, 22, 23, 24).

On the basis of the "hypothesis of exact orientation", Rice and Gershinowitz have calculated theoretically the absolute rates of the decompositions of methyl and ethyl nitrites. They arrive at a value of A of 2.4×10^{13} for both nitrites, which is in excellent agreement with the observed values, if the nature of the calculation be taken into consideration. However, the theory predicts the same value for both nitrites, and hence as yet offers no solution of the present problem. The theory is indeed closely related to the Kassel theory, as Rice and Gershinowitz have pointed out.

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